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(54) **AIR FILTERS COMPRISING POLYMERIC SORBENTS FOR ALDEHYDES**

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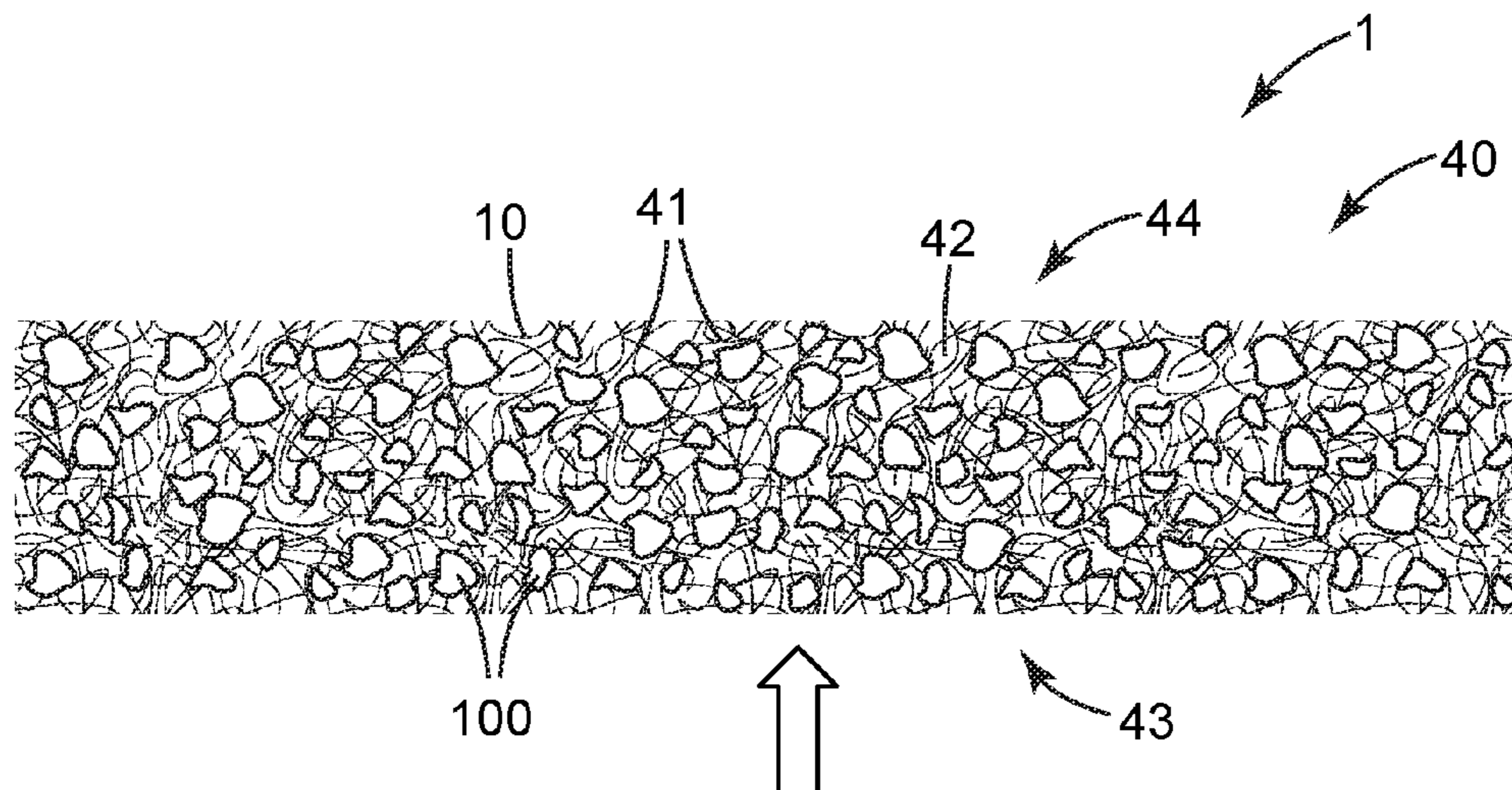
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(57) **ABSTRACT**

An air filter including a filter support that supports polymeric sorbent particles. The polymeric sorbent particles are the reaction product of a hydrolyzed divinylbenzene/maleic anhydride precursor polymeric material with a nitrogen-containing compound, with the nitrogen-containing compound being ionically attached to the hydrolyzed divinylbenzene/maleic anhydride.

**18 Claims, 4 Drawing Sheets**



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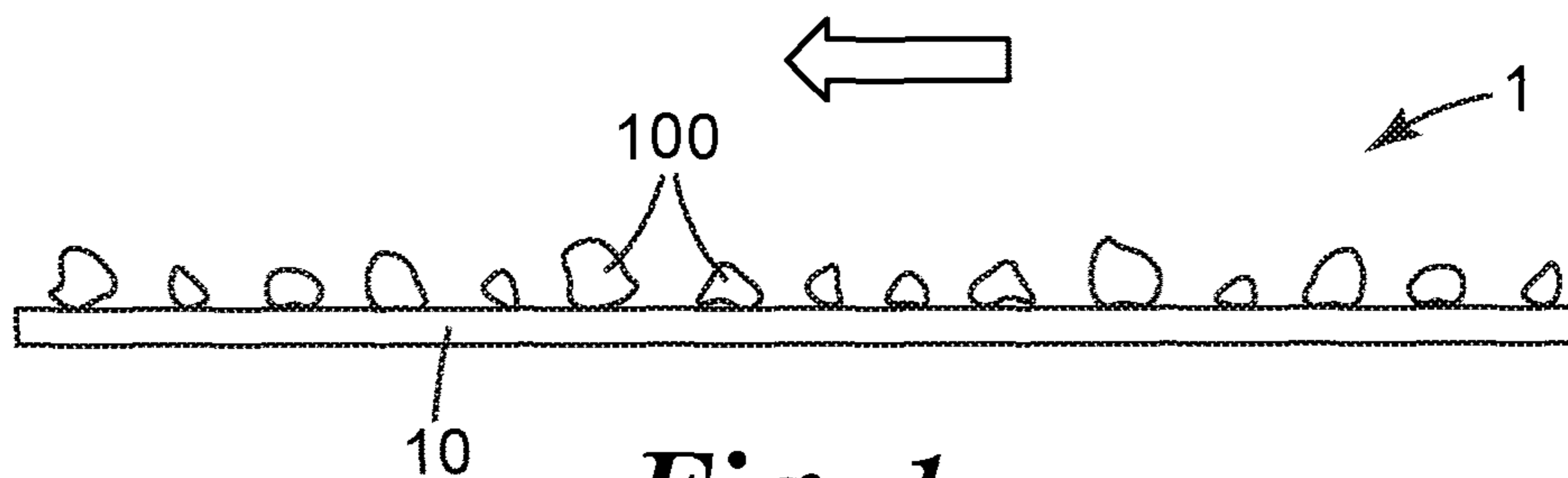
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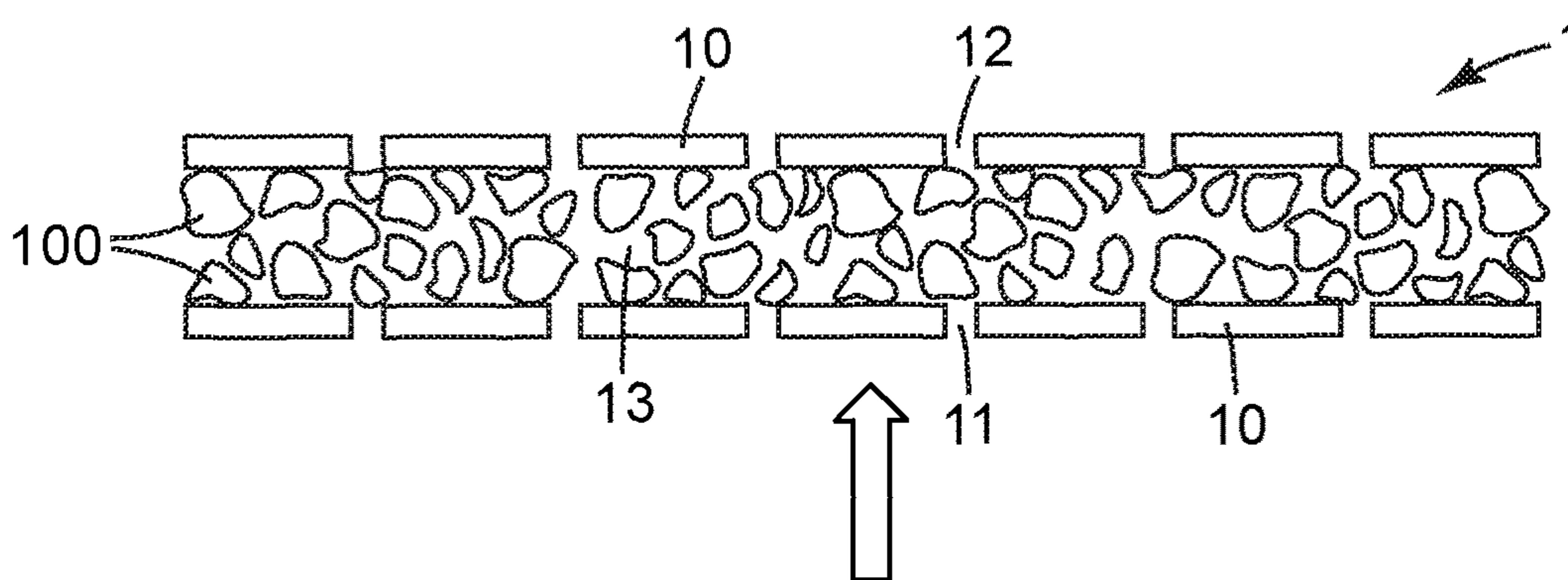
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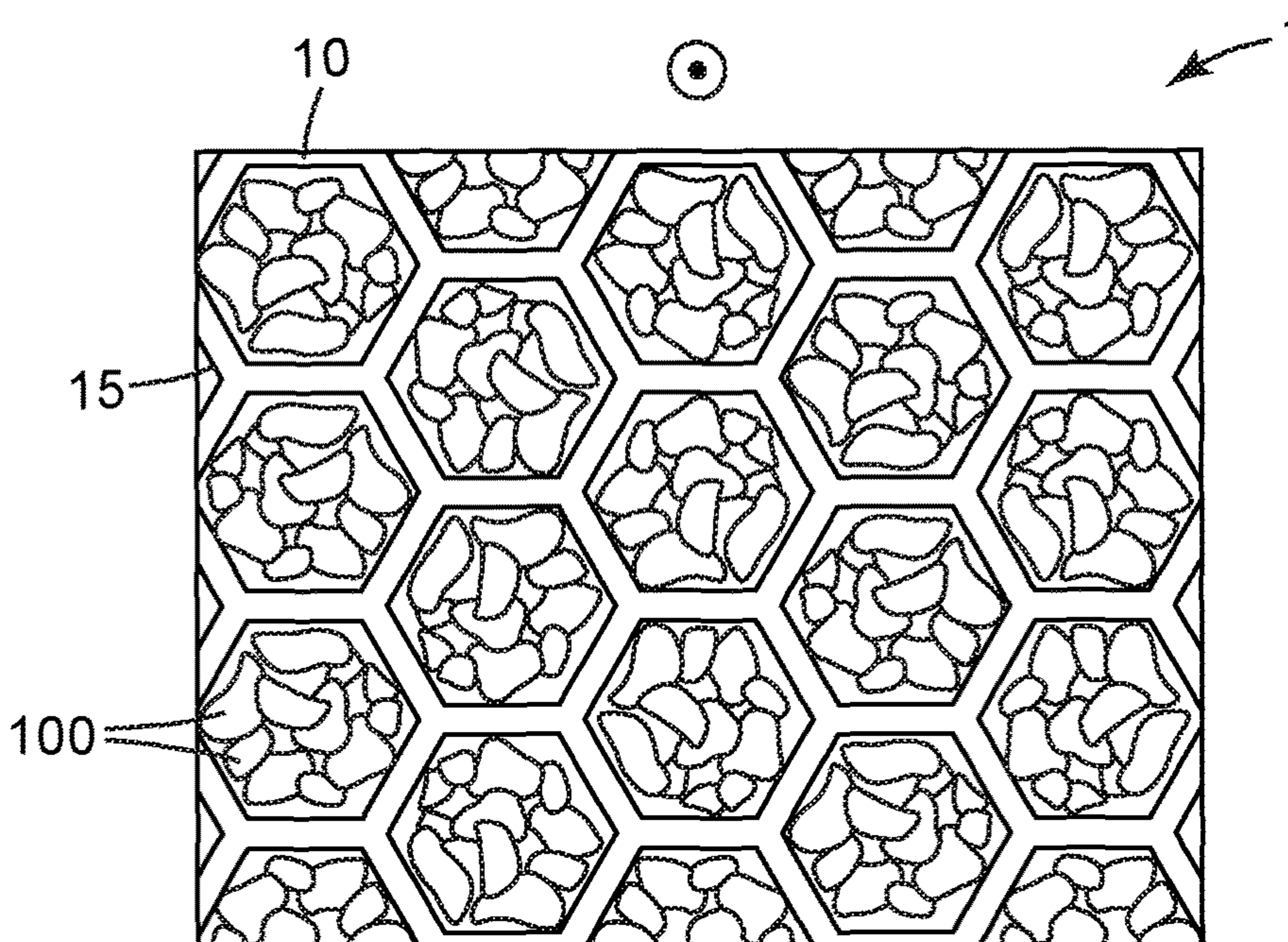
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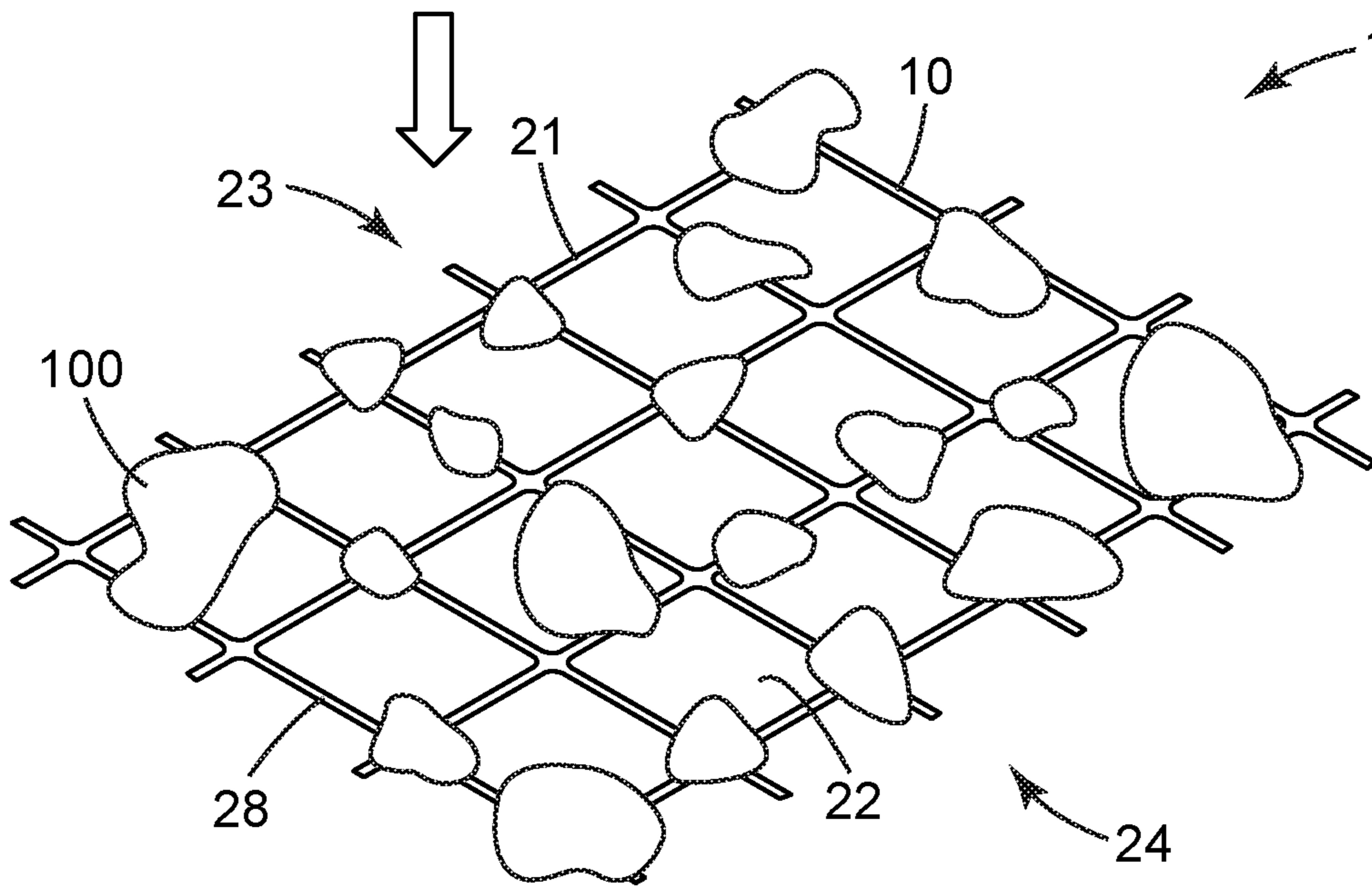
*Fig. 1*



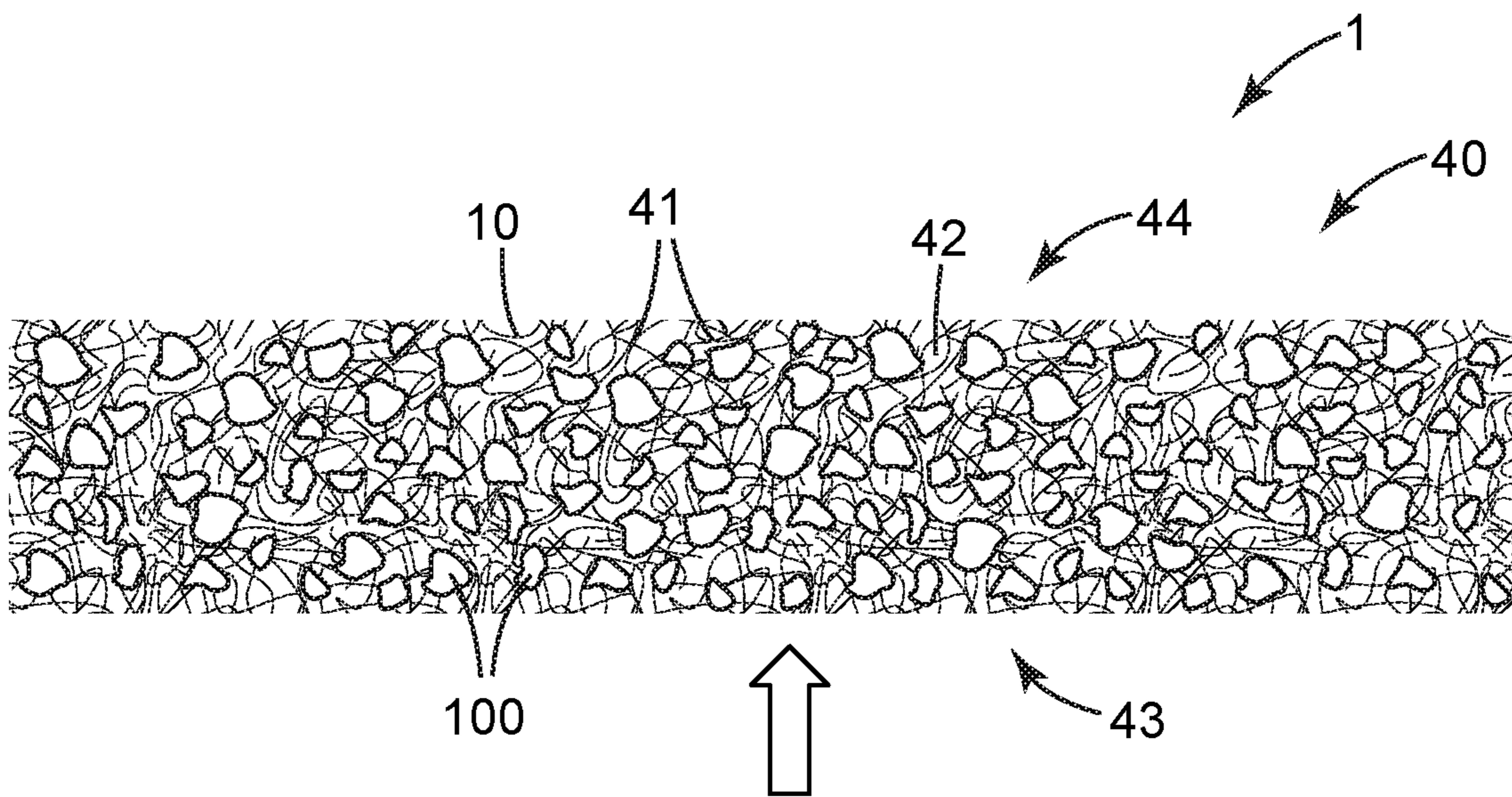
*Fig. 2*



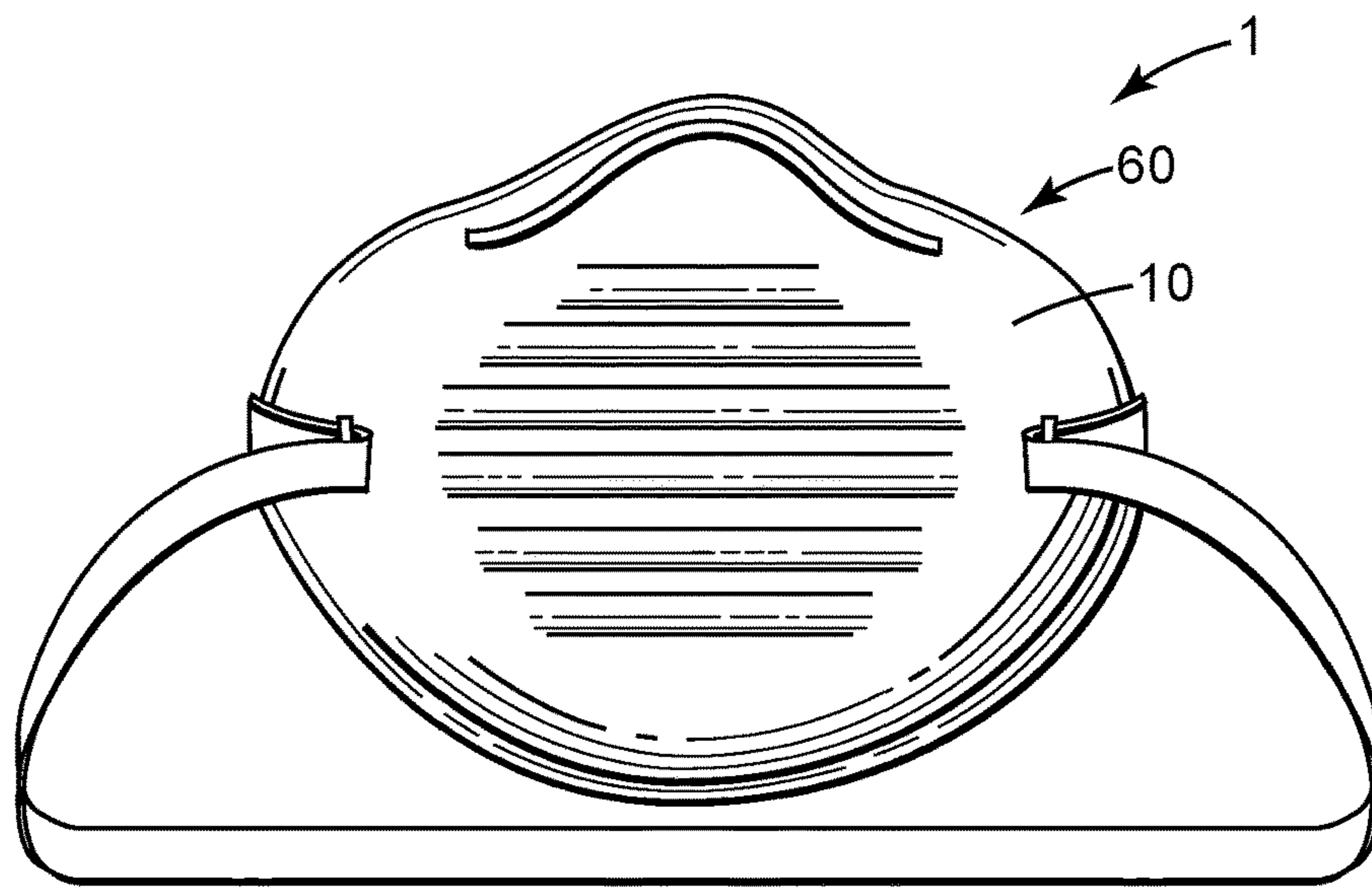
*Fig. 3*



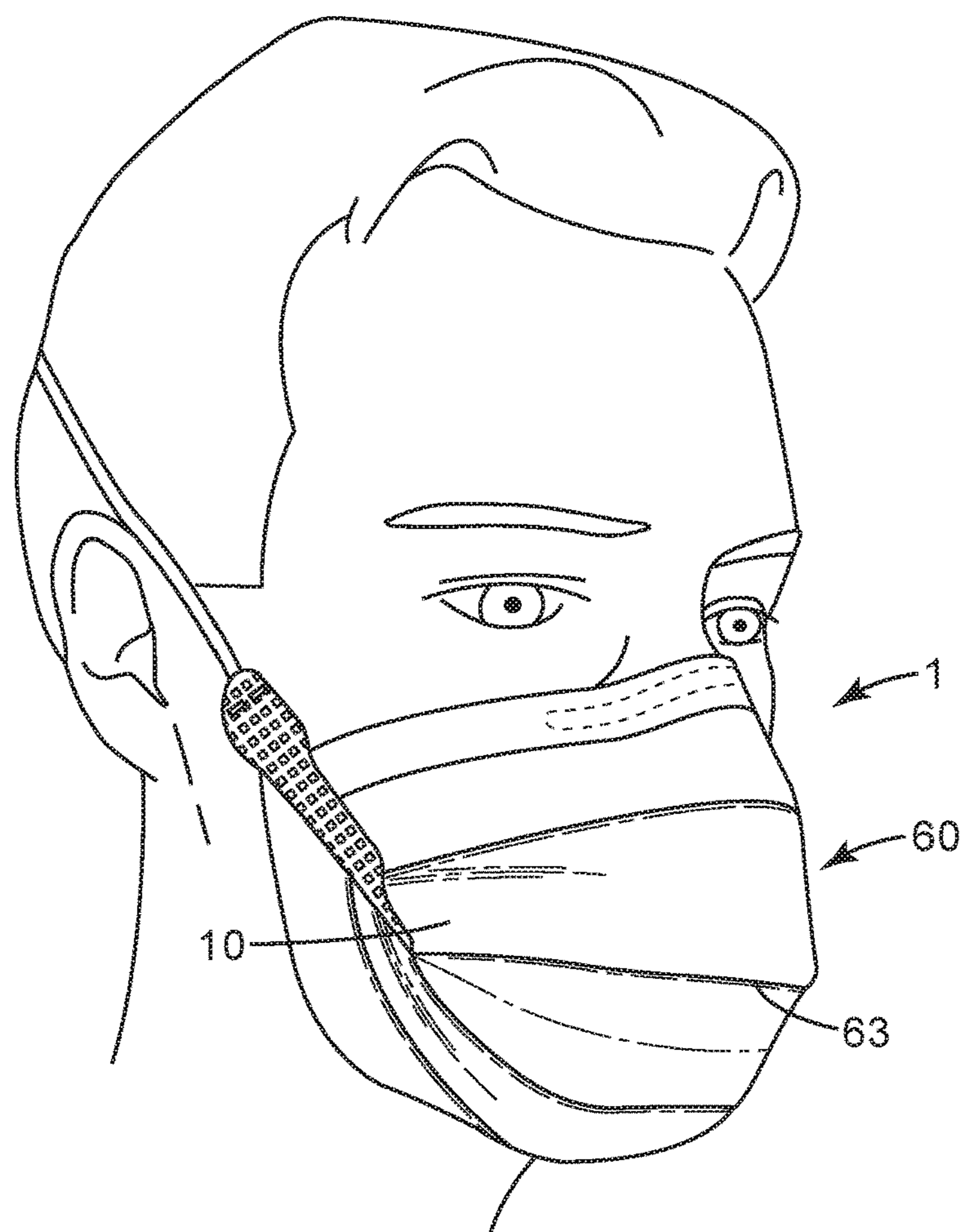
*Fig. 4*



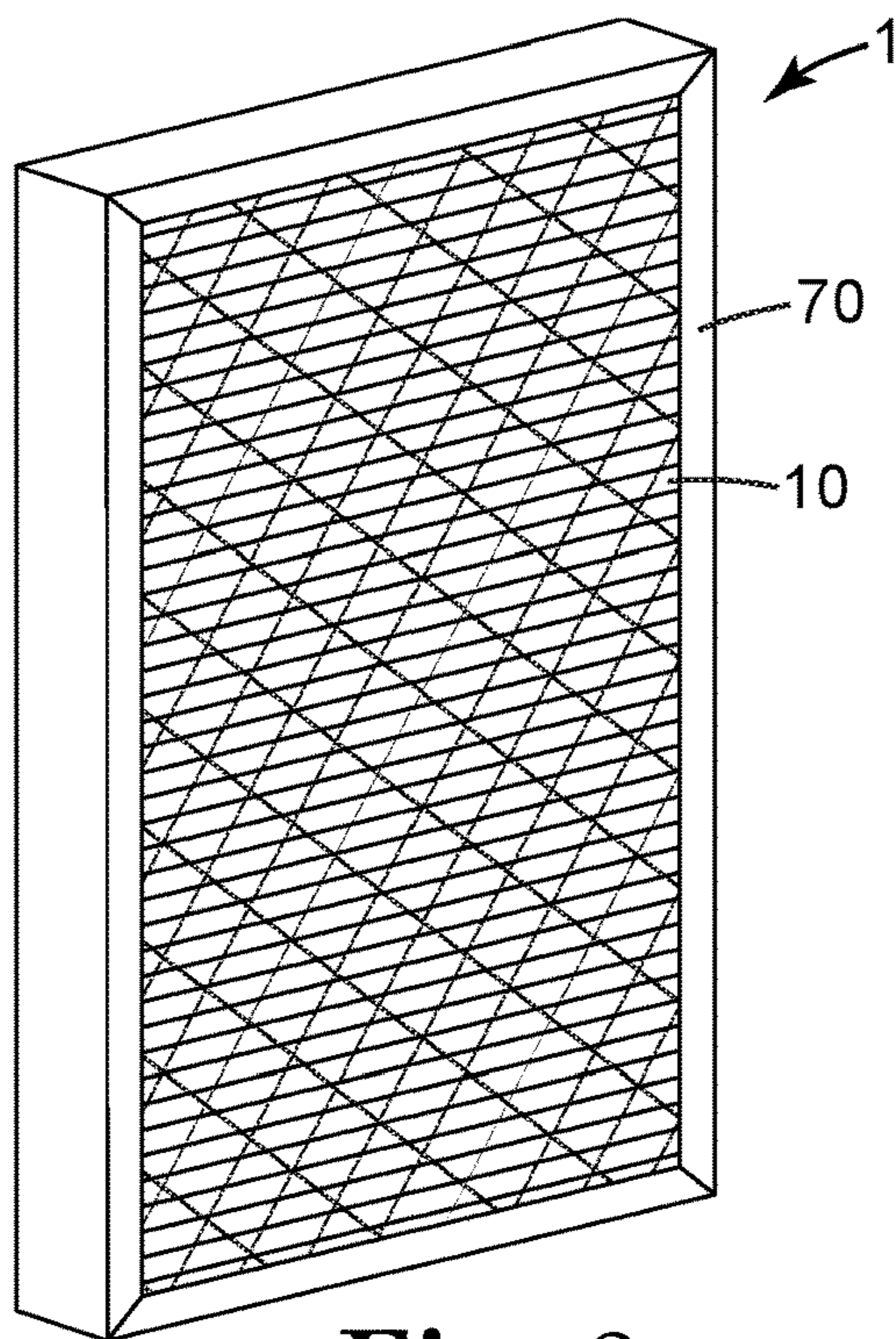
*Fig. 5*



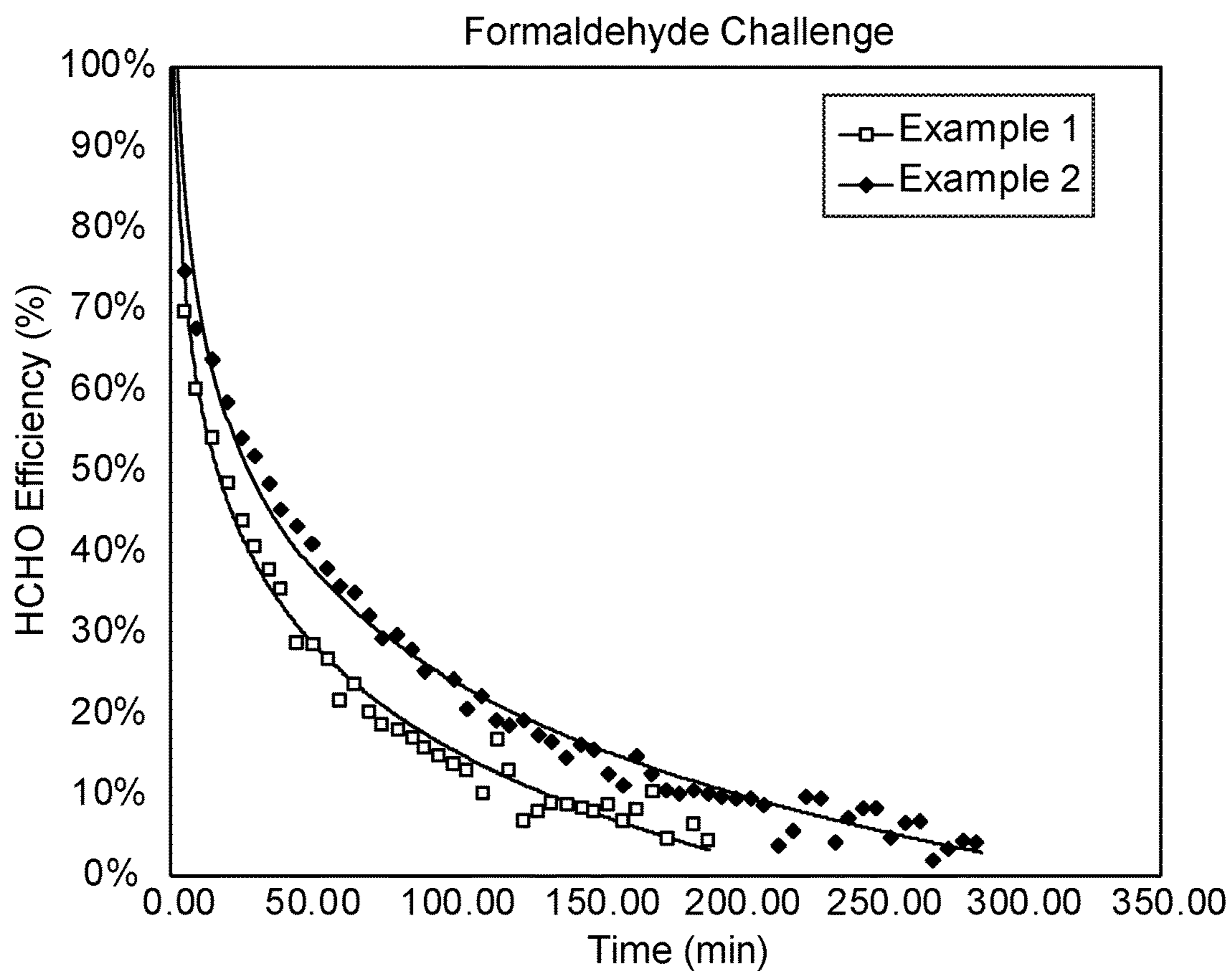
*Fig. 6*



*Fig. 7*



*Fig. 8*



*Fig. 9*

## AIR FILTERS COMPRISING POLYMERIC SORBENTS FOR ALDEHYDES

### CROSS REFERENCE TO RELATED APPLICATIONS

This application is a national stage filing under 35 U.S.C. 371 of PCT/IB2018/054064, filed Jun. 6, 2018, which claims the benefit of provisional Application No. 62/520,712, filed Jun. 16, 2017, the disclosure of which is incorporated by reference in its/their entirety herein.

### BACKGROUND

It is often desired to remove gaseous substances such as, e.g., formaldehyde, from air.

### SUMMARY

In broad summary, herein are disclosed air filters comprising filter supports that comprise polymeric sorbent particles. The polymeric sorbent particles are the reaction product of a hydrolyzed divinylbenzene/maleic anhydride precursor polymeric material with a nitrogen-containing compound, with the nitrogen-containing compound being ionically attached to the hydrolyzed divinylbenzene/maleic anhydride. These and other aspects will be apparent from the detailed description below. In no event, however, should this broad summary be construed to limit the claimable subject matter, whether such subject matter is presented in claims in the application as initially filed or in claims that are amended or otherwise presented in prosecution.

### BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 depicts a portion of an exemplary air filter comprising a filter support comprising sorbent particles as disclosed herein.

FIG. 2 depicts a portion of another exemplary air filter.

FIG. 3 depicts a portion of another exemplary air filter.

FIG. 4 depicts a portion of another exemplary air filter.

FIG. 5 depicts a portion of another exemplary air filter.

FIG. 6 depicts an exemplary respirator comprising a filter support comprising sorbent particles as disclosed herein.

FIG. 7 discloses another exemplary respirator.

FIG. 8 discloses a framed, pleated air filter comprising a filter support comprising sorbent particles as disclosed herein.

FIG. 9 presents formaldehyde challenge data for two Working Examples.

### DETAILED DESCRIPTION

#### Glossary

The term “air filter” denotes any apparatus or device in which a herein-described polymeric sorbent, supported by a filter support, is presented to air, e.g. a stream of moving air, so that a gaseous substance can be removed from the air. The term “filter support” denotes any structure that can retain sorbent particles and present them to, e.g., a stream of moving air, but that does not necessarily perform any filtration of microscopic particles from moving air. The term “filter media” denotes a filter support that is itself capable of filtering microscopic particles. A “microscopic” particle is a particle with an average diameter (or equivalent diameter, in the case of non-spherical particles) of less than 100 microns.

A “fine” particle is a particle with an average diameter or equivalent diameter of less than 10 microns.

The terms “polymeric sorbent” and “porous polymeric sorbent” are used interchangeably to refer to a polymeric material that is porous and that can sorb gaseous substances such as, for example, aldehydes. Porous materials such as the polymeric sorbents can be characterized based on e.g. the size of their pores. The term “micropores” refers to pores having a diameter less than 2 nanometers. The term “mesopores” refers to pores having a diameter in a range of 2 to 50 nanometers. The term “macropores” refers to pores having a diameter greater than 50 nanometers.

The term “upstream” is applicable to a circumstance in which a filter is exposed to moving air, and refers to the direction from which moving air encounters a filter; “downstream” refers to the direction in which filtered air exits a filter.

The term “netting” refers to a filter support that is comprised of relatively few layers (five or less, often one) of solid material, e.g. filaments.

The term “fibrous web” refers to a filter support that is comprised of numerous layers (e.g., more than five) of fibers.

The term “meltblown” refers to fibers (and the resulting fibrous webs) that are formed by extruding molten polymer streams into converging high velocity air streams introduced by way of air-blowing orifices located in close proximity to the extrusion orifices. The skilled person will appreciate that meltblown fibers and webs will characteristically exhibit features and signatures (e.g., differences in the orientation of the molecules of the material making up the fibers, as revealed e.g. by optical properties such as birefringence, melting behavior, and so on) by which such fibers and webs can be identified and distinguished from other types of web.

Disclosed herein is an air filter **1** as shown in generic representation in FIG. 1. Air filter **1** can be any apparatus or device that exposes herein-disclosed polymeric sorbent particles **100** to air, e.g. to a stream of moving air (with the general direction of airflow indicated in exemplary embodiment by the block arrow in FIG. 1 and in other Figures) so that a gaseous substance, e.g. an aldehyde such as formaldehyde, can be removed from the air.

Air filter **1** comprises at least one filter support **10**. A filter support **10** can be any structure that supports sorbent particles **100** in such manner that exposes them to air, while retaining the sorbent particles so that, if the air is moving, the sorbent particles are not dislodged by the moving air. If the air is moving, it may encounter individual sorbent particles while in laminar flow or while in turbulent flow, or may transition between flow regimes in, for example, passing through a collection of sorbent particles. In embodiments of one general type, filter support **10** may take the form of a substrate on which sorbent particles **100** are provided (e.g., are attached to a major surface thereof) and across which e.g. a moving stream of air may traverse, as shown in generic representation in FIG. 1. In some embodiments of this type, filter support **10** may retain sorbent particles **100** e.g. by way of the sorbent particles being attached (e.g., adhesively bonded) to the filter support. In embodiments of another general type, a filter support **10** may retain sorbent particles **100** e.g. by mechanically retaining the sorbent particles within the filter support, as shown in generic representation in FIG. 2. (In other words, in such embodiments the sorbent particles may not necessarily be attached to the filter support, but the filter support can physically block the sorbent particles from being dislodged and removed from the filter support.) In some embodiments,



a combination of mechanical retention, and attachment (e.g. bonding), of sorbent particles to the filter support may be employed.

In some embodiments, an air filter **1** may be (e.g., may consist essentially of) a filter support **10** comprising sorbent particles **100** (for example, a freestanding piece of such a filter support could be installed into e.g. a room air purifier). In other embodiments, an air filter **1** may comprise (in addition to the at least one filter support **10**) other layers as desired for any purpose, and/or may additionally comprise any other ancillary components such as e.g. a perimeter frame, one or more reinforcing or stabilizing members, one or more housing pieces, and so on. Various specific exemplary embodiments and arrangements are discussed in detail later herein.

As noted with reference to FIG. **1**, in some embodiments a filter support may take the form of a substrate (which substrate may be air impermeable, or air permeable) on a major surface of which sorbent particles **100** are disposed, e.g. attached. Air filters of this type may comprise, for example, a planar substrate bearing sorbent particles attached to a major surface thereof; a hollow tube with sorbent particles attached to an interior surface thereof; or, an array of flow-through channels provided by stacked or nested microstructured substrates (e.g., of the general type described in U.S. Pat. No. 7,955,570 to Insley) with sorbent particles attached to interior surfaces of the flow-through channels; and so on. In some embodiments sorbent particles **100** may be provided at least substantially as a monolayer on a surface of the substrate (e.g. as shown in FIG. **1**), except for such occasional stacking as may occur statistically e.g. in any industrial-scale deposition process.

With reference to FIG. **2**, the term filter support broadly encompasses any container that is designed to retain sorbent particles **100** therein and that includes at least one air inlet **11** for admitting air to the interior **13** of the container and at least one air outlet **12** to allow treated air to leave the container. Such supports of this general type may include well known filter cartridges in which sorbent particles **100** are retained within a cartridge housing made of e.g. one or more injection molded housing parts. In such filter cartridges, a single air inlet and/or outlet may be provided; or, a number of through-apertures may be provided in the filter cartridge housing to collectively provide an air inlet or outlet. Such through-apertures may be of appropriate size to prevent sorbent particles from passing therethrough; and/or, in some embodiments, an air-permeable protective layer (e.g., a screen or mesh) may be provided to ensure that the sorbent particles are retained within the cartridge housing. In some embodiments a filter support may be impermeable to air (e.g., may contain no through-apertures) in the locations of the support that are proximate to (e.g., that support and retain) sorbent particles, as in the design of FIG. **1**. In other embodiments, a filter support may be permeable to air (e.g., may include one or more through-apertures) in locations of the support that are proximate sorbent particles, as in the design of FIG. **2**. In some embodiments, a filter support in the form of a container (e.g., a filter cartridge) may be comprised of e.g. one or more injection molded housing parts that are assembled together and that may be air-impermeable except for the air inlet(s) and outlet(s). Such housing parts may be conveniently made of e.g. thermoplastic or thermoset polymers or copolymers chosen from e.g. polyamides, polystyrenes, ABS polymers, polyolefins, and so on. Such containers may also include ancillary components such as e.g. one or more resilient gaskets,

latches, splash guards, connectors (e.g. as needed for connecting the cartridge to e.g. a personal respiratory protection device) and so on.

It is emphasized that a filter support **10** that is in the form of a container (as in e.g. FIG. **2**) does not necessarily have to take the form of a rigid cartridge made e.g. of injection molded parts. Rather, in some embodiments such a container might take the form of e.g. two air-transmissive “walls” at least one of which is made of a relatively flexible material (e.g., a porous substrate such as a fibrous web, a perforated or microperforated flexible polymer film, and so on) with sorbent particles sandwiched between the two walls. Such a container (which may still be referred to in general as a filter “cartridge”) might take the form of e.g. a pouch or sachet.

Still further, the term filter support also broadly encompasses any porous, air-permeable material on which or within which sorbent particles **100** are disposed. (By a porous, air-permeable material is meant a material comprising internal porosity that is interconnected so as to allow airflow through the material, as distinguished from e.g. a closed cell foam.) Such materials might be e.g. open-celled foam materials of any suitable type; or, such a material might be a microporous membrane; for example, a phase-inversion membrane, a track-etch membrane (e.g., of the type exemplified by various products available from Whatman under the trade designation NUCLEPORE); or, a stretch-expanded membrane (e.g., of the type exemplified by various products available from W.L Gore and Associates under the trade designation GORE-TEX and available from Celgard corporation under the trade designation CELGARD.) It will be appreciated that filter supports **10** of this general type are not limited to being used e.g. in pairs so as to define a space therebetween as described above. Regardless of the specific mode of use, such a filter support **10** may, in some embodiments, take the form of a sheet-like material that exhibits a major plane and that exhibits a thickness of less than about 8, 5, 3, or 1 mm and that is configured to allow airflow therethrough at least in a direction at least generally perpendicular to the major plane of the sheet-like material.

From the above discussions it will be appreciated that a filter support as disclosed herein widely embraces any material or arrangement, in any form or geometric shape (and whether consisting e.g. of a single entity such as a nonporous substrate, an air-permeable netting, or a porous foam, or made of an assembled combination of parts that collectively form a filter cartridge), that can present sorbent particles to air, e.g. to a stream of moving air. In some embodiments a filter support can be configured so that moving air may flow e.g. at least generally parallel to a major surface of the support that bears sorbent particles (e.g., as in the arrangement of FIG. **1**). In some embodiments the moving air may flow at least generally perpendicular to a major surface of the support (e.g., as in the arrangement of FIG. **2**). In some embodiments, moving air may flow in directions intermediate between these two extremes. In some embodiments, airflow in both directions and/or in directions intermediate between these two extremes, may occur e.g. in different portions of the air filter.

In embodiments of the general type illustrated in exemplary manner in FIG. **3**, an air filter **1** may comprise a filter support **10** that is in the form of a “honeycomb” **15**. The skilled person will recognize a honeycomb as being a flow-through support structure that comprises numerous macroscopic through-apertures that allow airflow therethrough, the apertures being separated from each other by partitions (walls) of the honeycomb structure. (While the

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term honeycomb is used here for convenience, the skilled person will appreciate that the structure may be of any geometry (e.g., with apertures that are square, triangular, round, etc.) and may exhibit a somewhat irregular appearance rather than being limited strictly to the regular hexagonal geometry shown in the exemplary design of FIG. 3). Often, such honeycombs may comprise through-apertures with rather large diameter or equivalent diameter (e.g. from 10-15 mm), in contrast to the above-described stacked microstructured substrates, which may often comprise flow-through channels with a diameter or equivalent diameter of only e.g. a few mm or smaller. The walls of the honeycomb may be made of any suitable material, e.g. molded or extruded plastic, paperboard or cardboard, metal, and so on.

In some embodiments, sorbent particles may be attached to interior walls that define the apertures of the honeycomb. However, in some embodiments, it may be convenient to partially, or at least substantially, fill the apertures of the honeycomb with sorbent particles (to the extent permitted by packing behavior, depending e.g. on the average size, size distribution, and shape of the sorbent particles) as in FIG. 3. In such a case the honeycomb may be provided with upstream and downstream air-permeable substrates (e.g., suitable meshes or screens) that allow airflow to enter and exit the through-apertures of the honeycomb and yet retain the sorbent particles within the through-apertures of the honeycomb. (The direction of airflow in the exemplary honeycomb of FIG. 3 is out-of-plane as indicated by the circle/dot arrow.) In some embodiments, the sorbent particles may be packed loosely within the apertures e.g. so that the particles are able to move or shift slightly. In other embodiments, the sorbent particles may be bonded to each other (e.g., by use of an adhesive, a heat-activated binder, etc., in amounts sufficient to bond particles to each other at contact points but not in amounts that would unacceptably occlude the particles so as to impact their ability to capture gaseous substances) e.g. so as to minimize shifting or settling of the particles within the apertures. In other words, in some embodiments (not necessarily limited to use in honeycombs) sorbent particles **100** may be provided in the form of a monolithic, air-permeable block (of any desired size and shape) collectively provided by an aggregation of particles that are bonded together, rather than being provided as individual particles. Exemplary methods of making such monolithic structures (which again, may have any suitable size and shape for incorporation into any desired air filter, for example, for fitting into a container such as e.g. a cartridge or canister, or for forming a layer of e.g. a respirator) are discussed e.g. in U.S. Pat. No. 5,033,465 to Braun. Methods of bonding sorbent particles together to make, in particular, a structure that is at least semi-flexible (and thus may be particularly suited for use in e.g. a flexible respirator mask), are discussed e.g. in U.S. Pat. No. 6,391,429 to Senkus.

The skilled person will appreciate that there may not necessarily be a firm dividing line between some of the above-mentioned embodiments (for example, between sorbent particles being provided within hollow tubes, versus being provided within channels defined by a stacked microstructured substrate, versus being provided within apertures of a honeycomb). All such designs and arrangements, and combinations thereof, are encompassed within the general concept of an air filter that comprises one or more filter supports as disclosed herein. It is noted in particular that in some embodiments, an air filter **1** as disclosed herein can comprise sorbent particles that are partially filled, or at least substantially filled, into the interior of any suitable container

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(of any geometric form and made of any material, whether e.g. rigid or at least semi-flexible) so as to form e.g. a packed bed. In some embodiments, such a container might take the form of a hollow tube, e.g. a tube resembling the gas-detection tubes often referred to as Drager tubes.

In some embodiments, a filter support **10** may comprise a thin, sheet-like material with numerous through-apertures **22** that allow airflow therethrough, as shown in exemplary, generic representation in FIG. 4. In various embodiments, filter support **10** may take the form of any suitable netting, mesh, screen, scrim, woven or knitted material, meltspun material, microperforated film, and so on. The term netting will be used herein for convenience in describing any such material, that is comprised of relatively few layers (five or less; often, a single layer as in FIG. 4) of filaments (or, in general, layers of solid material in between through-openings). Often, such filaments (or solid portions of a sheet-like filter support material, e.g. a microperforated film) are relatively large (for example, 0.1, 0.2, or 0.5 mm or more) in diameter or the equivalent thereof. Such a netting may be comprised of any suitable material, e.g. an organic polymer, an inorganic material (e.g., glass or ceramic), or a metal or metal alloy.

In such embodiments airflow may occur primarily through the through-apertures **22** between the solid portions **21** (e.g. filaments) of the netting so that the airflow is oriented at least generally perpendicular to the support; however, if desired the airflow could occur at least generally parallel to the netting. In the case of generally perpendicular airflow that passes through the netting, it may be convenient that the sorbent particles are positioned on the upstream side **23** of the netting (as in FIG. 4). However, if desired the sorbent particles may be positioned on the downstream side **24** of the netting. In particular embodiments, sorbent particles may be positioned on both sides of the netting. In some embodiments, a netting (or, in general, any sufficiently air-permeable substrate) comprising sorbent particles may be used "open-face" as in the illustrative embodiments of FIGS. 1 and 4. In other embodiments, a secondary retaining layer that is sufficiently air-permeable (e.g., a second layer of netting, or a layer of a fibrous web, a microporous membrane, or the like) may be positioned atop the sorbent particles to assist in retaining the sorbent particles in position. (In other words, the sorbent particles may be sandwiched between the netting and a secondary retaining layer.)

In many embodiments, sorbent particles **100** may be bonded, e.g. adhesively bonded, to the solid material (e.g., filaments) of the netting, e.g. by way of an adhesive, e.g. a pressure-sensitive adhesive, a hot-melt adhesive, an epoxy adhesive, and the like **28** that is provided on at least one major surface of one side of the netting. Sorbent particles may each be bonded e.g. to a single filament, or may be bonded to multiple filaments. The average diameter of the filaments, and the average size of the through-apertures between the filaments, can be chosen in view of the average size of the sorbent particles if desired. In various embodiments, such nettings may exhibit an average filament diameter in the range of e.g. 0.2 mm to about 2.0 mm. In various embodiments, the openings of the netting may range from e.g. about 0.5 mm in shortest dimension to about 5 mm in longest dimension, and may be chosen in view of the particle size of the sorbent. By way of specific example, a netting with openings in a range of about 1-2 mm may be well suited for use with a sorbent that exhibits a particle size in the range of 8x20 mesh. Exemplary nettings that might be suitable for use as disclosed herein include various products available from Delstar Technologies; for example, the products avail-

able under the trade designations KX215P, R0412-10PR, RB0404-10P, N02014-90PP, RB0404-28P, N03011-90PP, and TK16-SBSH.

In particular embodiments, a suitable pressure sensitive adhesive **28** may be provided on a major surface of the netting (in other words, the pressure-sensitive adhesive may be provided on surfaces of the filaments that collectively provide that major surface of the netting). This may be done e.g. by coating a pressure-sensitive adhesive precursor onto the netting and then transforming the precursor into a pressure-sensitive adhesive. The precursor may be e.g. a solution in an organic solvent(s), an emulsion, a hot-melt composition, and so on. Such a precursor may be transformed e.g. by drying to remove solvent and/or water, by cooling to solidify a hot-melt composition, and so on. The deposition and transformation should be done in such manner as to avoid unacceptably filling or clogging the through-apertures of the netting (unless the airflow is not to pass through the netting in ordinary use of the filter).

It will be appreciated that in some embodiments particles that are disposed on a netting may be attached to the netting primarily due to e.g. adhesive bonding (rather than through e.g. mechanical entanglement). In some embodiments, the sorbent particles may be present on a filter support at least substantially in the form of a monolayer. In other embodiments sorbent particles may be present in multiple layers (made e.g. by adhesively bonding a first layer of sorbent particles to a major surface of a netting, applying additional adhesive atop the first layer of sorbent particles, depositing more sorbent particles, and repeating the process to build up a collection of sorbent particles of any desired depth).

In some embodiments a filter support **10** may comprise a sheet-like material comprised of numerous fibers, often entangled with each other and often present in numerous "layers" (e.g., more than five layers) as shown in exemplary embodiment in FIG. **5**. The term fibrous web will be used herein for convenience in describing any such material. It will be appreciated of course that due to the random nature of many such fibrous webs, the fibers may not necessarily be, and often will not be, present in discrete layers (e.g., layers that can be peeled apart from each other); however, it will be readily apparent if e.g. five or more separate fibers or sections of fibers are encountered in traversing the thickness (depth) of such a web from a first major surface **43** thereof to a second major surface **44** thereof (as in FIG. **5**). Any material exhibiting such a fiber arrangement falls under the definition of a fibrous web as used herein.

Often, such fibers may be relatively small (for example, less than 100, 80, 60, 40, 20, 10, 5, or 2  $\mu\text{m}$ ) in diameter or the equivalent thereof. Mixtures of fibers of various diameters may of course be used. Such a fibrous web may be any suitable type of web, e.g. a nonwoven web in which the fibers are relatively randomly arranged (e.g. except for such partial amounts of fiber alignment as may occur with e.g. carded webs and with certain types of fiber-deposition methods). Alternatively, such a fibrous web may be comprised of a knitted or woven web in which the fibers are provided in a sufficient number of layers. Typically, air will flow through the web by passing through interstitial spaces between the numerous fibers of the web; often, such airflow is oriented at least generally perpendicular to a major plane of the fibrous web as in FIG. **5**. However, if desired the airflow could occur at least generally parallel to a major plane of the fibrous web. The fibers of such a fibrous web can be bonded to each other (so that the web has sufficient mechanical integrity to be processed and handled) in any suitable manner. Such bonding methods might be chosen

from e.g. hydroentangling, needle-punching, calendering, and the like. In some embodiments, the fibers may be autogenously bonded to each other, meaning that the fibers are bonded at an elevated temperature as obtained in an oven or with a so-called through-air bonder without application of solid contact pressure such as in point-bonding or calendering. In particular embodiments, the fibers may be bonded using autogenous bonding methods of the general type described in U.S. Pat. No. 7,947,142 to Fox (in which a stream of heated air is passed through the collection of fibers followed by forceful quenching). Or, one or more binders (whether in the form of fibers, solid particles, a water-born emulsion, and so on) may be added and then activated (e.g. by heating) to bond the fibers together to form the final web. Any such bonding operation (whether achieved primarily mechanically by entanglement of fibers, or by use of a melt-bonding of fibers and/or by use of an added binder) may additionally serve to bind sorbent particles into or onto the web, as noted below.

In some embodiments sorbent particles may be deposited primarily, or exclusively, on a major surface (e.g., a major upstream surface) of the fibrous web, in somewhat similar manner to the arrangement of particles on the netting of FIG. **4**. In some embodiments at least some of the sorbent particles may penetrate at least partly into the interior of the fibrous web. (This is in contrast to the situation with a netting provided by e.g. a monolayer of filaments as in FIG. **4**, in which case the support exhibits little or no "interior" into which sorbent particles could penetrate.) In some such embodiments the sorbent particles may be found primarily in the region of the fibrous web proximate the major surface onto or into which the sorbent particles were deposited. In many embodiments, however, it may be desirable to provide that sorbent particles **100** are distributed widely throughout the thickness of the fibrous web (as shown in exemplary embodiment in FIG. **5**), as opposed to the particles being e.g. deposited onto one surface so that they either remain on the surface or only penetrate a short distance into the interior of the fibrous web. Suitable methods of forming fibrous webs with sorbent particles distributed widely (e.g., randomly) throughout the interior of the web are discussed later herein.

In particular embodiments, a fibrous web filter support may be a nonwoven web. By definition, nonwoven fibrous webs do not encompass e.g. woven or knitted webs or microperforated films. Such a web can be made by any suitable method and can be of any suitable type. For example, such a nonwoven web might be: a carded web; a wet-laid web (made e.g. by papermaking processes); a dry-laid web made e.g. by a conventional airlaying process such as the well-known Rando-Webber process, or made by a specialized process such as the gravity-laying process described in U.S. Pat. No. 8,834,759 to Lalouch; or, a meltspun web (e.g. a spunbonded web, a spunlaced web, and so on). (It will be appreciated that certain e.g. spunbonded or spunlaced webs may qualify as nettings rather than as fibrous webs, depending e.g. on the depth of fibers that are laid down.) In particular embodiments, the nonwoven web may be a meltblown web, which process and resulting web will be well known to the skilled person. Any combination of layers of these various materials (including combination with layers that are not nonwoven webs) can be used. The fibers may be made of any suitable material, e.g. thermoplastic organic fibers (such as e.g. polyolefin fibers, cellulosic fibers, polyester fibers, nylon fibers, etc.), inorganic fibers (such as e.g. fiberglass or ceramic fibers), metal fibers, and so on.

Sorbent particles may be provided on and/or within a porous material, e.g. a fibrous web such as a nonwoven web to form a herein-disclosed filter support of an air filter, by any suitable method. In some embodiments, the sorbent particles may be deposited on or into a pre-existing fibrous web. For example, in some embodiments a nonwoven web may comprise one or more binding components such as bondable fibers and/or a non-fibrous binder (a non-fibrous binder may take the form of e.g. particles, an emulsion or latex, and so on). The web may be heated to a temperature to soften and activate such a binding component(s), and the sorbent particles may then be deposited onto a major surface of the nonwoven web to be bonded thereto. It will be appreciated that many such processes may preferentially result in sorbent particles being present on or proximate a major surface of the nonwoven web onto which the sorbent particles were deposited. If desired, such a process may be repeated multiple times with the successive layers being bonded together to form a multilayer product comprising sorbent particles therein.

In other embodiments, the sorbent particles may be introduced into a nonwoven web during the process of making the web. For example, if a nonwoven web is made by meltblowing, it may be convenient to introduce the sorbent particles into the flowing stream of incipient fibers (the term incipient fibers refers to molten streams that may or may not have begun to solidify into fibers, or finished solidifying into fibers). General methods of performing such operations are disclosed in US Patent Application Publication No. 20120272829 to Fox, which is incorporated by reference herein. The incipient fibers may be deposited (e.g., onto a temporary collection surface or onto a secondary web that remains as part of the filter support) in a condition in which the incipient fibers are at least slightly sticky (bondable). Such arrangements can provide that at least some of the fibers of the meltblown nonwoven web are bonded (e.g., melt-bonded) to the sorbent particles. In this manner a meltblown web can be made comprising sorbent particles therein, in a single operation.

Of course, it is also possible to use other methods to introduce sorbent particles into a mixture of fibers prior to the fibers being collected as a web. For example, sorbent particles may be mixed with fibers that are input to a web-formation process (e.g., the above-mentioned gravity-laying web-formation process), to form a collected mass of fibers comprising sorbent particles therein. Such an approach can include adding binder (whether in the form of fibers, or as non-fibrous binders such as particles, an emulsion, etc.) to the input materials so that the collected mass of fibers can be heated to bind the fibers together to form a web and/or to bond the sorbent particles into the web. Whatever approaches is/are used, the primary mechanism by which sorbent particles are bound into or onto the fibrous web can be the same or different from the binding mechanism that is used to bind the fibers together to form the web.

With particular regard to a meltblown fibrous web, a variety of fiber-forming polymeric materials may be used to form such fibers. At least some fibers may be made of a material that exhibits sufficient bonding (adhesive) properties under the conditions (e.g., melt-blowing conditions) used in making the nonwoven web. Examples include thermoplastics such as polyurethane elastomeric materials, polybutylene elastomeric materials, polyester elastomeric materials, polyether block copolyamide elastomeric materials, polyolefin-based elastomeric materials (e.g., those available under the trade designation VERSIFY from Dow), and elastomeric styrenic block copolymers (e.g., those available

under the trade designations KRATON from Kraton Polymers, Houston, Tex.). Multicomponent fibers (e.g., core-sheath fibers, splittable or side-by-side bicomponent fibers and so-called "islands in the sea" fibers) in which at least one exposed surface of the fibers (e.g., the sheath portion of a core-sheath fiber) exhibits sufficient adhesive properties, may also be used.

In some embodiments, fibers that are able to bond to sorbent particles **100** may be the only fibers present in the meltblown web. In other embodiments, other fibers (e.g. that do not participate to any significant extent in bonding the sorbent particles) may be present e.g. as long as sufficient bondable fibers are present. In various embodiments, bondable fibers may comprise at least about 2 weight percent, at least about 4 weight percent, and at least about 6 weight percent of the meltblown nonwoven web. In further embodiments, bondable fibers may comprise no greater than about 20 weight percent, no greater than about 17 weight percent, and no greater than about 15 weight percent of the meltblown nonwoven web. Any nonbondable fibers that are present in the web may be of any suitable type and composition; for example, any of the well known polyolefinic fibers (e.g. polypropylene, polyethylene, and the like) may be used, as may any of the well known polyester fibers. In at least some embodiments, the nonwoven web is essentially free of any added binder of any kind. That is, in such cases essentially all binding of the sorbent particles (to retain them in the meltblown nonwoven web) is performed by the bondable fibers. Such embodiments thus exclude the presence of binder in such forms as particles or powders, liquids such as latexes, emulsions, suspensions, or solutions, and so on.

It will be appreciated that the above discussions have concerned methods in which bonding of fibers to the sorbent particles is at least partially used to retain the particles within the nonwoven web. Physical entanglement of the sorbent particles within the fibers can also assist in retaining the sorbent particles within the nonwoven web. In some embodiments, a secondary air-permeable layer (e.g. a scrim or facing) can be applied to (e.g., bonded to) one or more major surfaces of the nonwoven web to minimize the chances of any of the sorbent particles becoming dislodged therefrom. In fact, in some embodiments it may be convenient to deposit the incipient fibers that will form a meltblown nonwoven web (along with the sorbent particles that are merged into the stream of incipient fibers), onto a major surface of a secondary web (e.g., scrim or facing) so that the meltblown web is bonded to the secondary web in the act of making the meltblown web.

In some embodiments, air filter **1** may comprise at least one filter media **40**. A filter media is a filter support **10** that can retain sorbent particles **100** and expose them to air; beyond this, a filter media is a particular type of filter support that is capable of filtering significant amounts of microscopic particles (i.e., particles of average diameter of 100 microns or less) from moving air. A filter media **40** may comprise any material that can provide an air-permeable network structure into or onto which sorbent particles can be incorporated so as to present the sorbent particles to an airstream that is moving through the air-permeable network structure, and that furthermore is itself capable of filtering microscopic particles. Such a filter media might be e.g. a nonwoven web that is a meltblown and/or charged web.

As noted, a filter media is able to capture a significant amount of microscopic particles (with diameter 100  $\mu\text{m}$  or less). In specific embodiments, a filter media may be able to capture a significant amount of fine particles in the range of

e.g. 10  $\mu\text{m}$  or less, or even in the range of 2.5  $\mu\text{m}$  or less. In particular embodiments, the filter media may be capable of performing HEPA filtration. It will be appreciated that use of electret (charged) materials as described below, may substantially enhance the ability to perform e.g. fine-particle filtration or HEPA-filtration. In various embodiments, a filter media **40** may exhibit a Percent Penetration (specified herein as using Dioctyl Phthalate as a challenge material, and tested using methods described in U.S. Pat. No. 7,947,142 to Fox) of less than about 80, 70, 60, 50, 40, 30, 20, 10, or 5. All processes (e.g., fiber-bonding, charging, pleating, and the like), parameters and characterizations that are described herein with respect to filter supports in general, may be applied in particular to filter media.

In some embodiments, a nonwoven web (e.g., a melt-blown nonwoven web) for use as a filter support (or, in particular, as a filter media) may include electrostatically charged fibers. Charging of such fibers may be done by any suitable method, for example, by imparting electric charge to the nonwoven web using water as taught in U.S. Pat. No. 5,496,507 to Angadjivand, or as taught in U.S. Patent Publication No. 2009/0293279 to Sebastian. Nonwoven electret webs may also be produced by corona charging as described in U.S. Pat. No. 4,588,537 to Klaase, or using mechanical approaches to impart an electric charge to fibers as described in U.S. Pat. No. 4,798,850 to Brown. Any combination of such approaches may be used. Fibers may be charged before being formed into the nonwoven web, or after the nonwoven web is formed. (In any case, any such charging may be conveniently performed before the air filter media is pleated, if it is to be pleated.) In the case that an air filter is to include a particle-filtration layer that is a different layer from filter support **10** (as described below), such a particle-filtration layer may be charged if desired, e.g. by any of the above approaches.

If the filter support (whether free-standing, or part of a multilayer assembly) is to be pleated, pleat formation and pleat spacing may be performed using any suitable technique including those disclosed in U.S. Pat. No. 4,798,575 to Siverson, U.S. Pat. No. 4,976,677 to Siverson, and U.S. Pat. No. 5,389,175 to Wenz. Pleating procedures that may be useful are also described e.g. in U.S. Pat. No. 7,235,115 to Duffy. (It will be appreciated, however, that in at least some embodiments the use of score-pleating may be avoided since the scoring process may serve to crush at least some of the sorbent particles.) In various embodiments, the pleated air filter support may include about 0.5 to about 5 pleats per 2.5 centimeters. More specifically, the pleat spacing may be e.g. from about 6, 8, 10, or 12 mm, to about 50, 40, 30, 20, or 15 mm. In various embodiments, the pleat height may be e.g. from about 15, 20, 25, or 30 mm, to about 100, 80, 60 or 40 mm.

An air filter **1** may comprise a filter support **10** (which by definition supports at least some polymeric sorbent particles **100**) that consists of a single layer; or, multiple layers of filter support **10** (e.g., each layer including at least some polymeric sorbent particles **100**) may be present in an air filter **1**. Particularly if the filter support(s) **10** is not itself an air filter media as defined herein, the air filter **1** may include (in addition to the at least one filter support layer **10**) one or more particle-filtration layers (e.g., capable of filtration of microscopic particles, fine particles, and/or HEPA filtration) that do not include polymeric sorbent particles **100**. Such a particle filtration layer may be electrostatically charged if desired, and in various embodiments may exhibit a Percent Penetration of less than about 80, 70, 60, 50, 40, 30, 20, 10, or 5. (The term particle broadly encompasses e.g. aerosols,

dust, mist, fumes, smoke, mold, bacteria, spores, pollen, and so on.) In particular embodiments, such a particle-filtration layer may be a high-loft spunbonded nonwoven web e.g. of the type described in U.S. Pat. No. 8,240,484 to Fox, and comprising a solidity of from less than 8%, to about 4%, and that is comprised of meltspun fibers that are substantially free of crimped fibers, gap-formed fibers and bicomponent fibers.

Regardless of whether or not any particle-filtration layers are present, an air filter **1** may comprise (in addition to at least one filter support layer **10** and any optional particle-filtration layers) one or more secondary layers (e.g., scrim, nettings, covers, and so on), e.g. to serve as a cover layer, a coarse prefilter, a carrier layer, a skin-contacting layer, to provide mechanical support or stiffness, and so on. That is, in general, and without regard to the particular type, configuration or construction of a filter support layer **10**, such a filter support layer may be provided as one layer of a multilayer air-permeable assembly (stack) that can collectively provide an air filter **1**. Any such multilayer stack may of course be pleated, framed, and so on, as described herein.

The herein-disclosed sorbent particles (whether e.g. dispersed within a nonwoven fibrous web, disposed on a surface of a substrate, filled into a receptacle(s) e.g. to form a packed bed, etc.), may be used in combination with any secondary sorbent particles, configured to capture any desired component present in air (e.g. a noxious gas/vapor). In some embodiments, such secondary sorbent particles may be present in a separate layer that is e.g. upstream or downstream of polymeric sorbent particles **100**. In other embodiments, sorbent particles **100** and any desired secondary sorbent particle(s) may be mixed together. Secondary sorbent particles (whether used in a separate layer or as a commingled mixture with polymeric sorbent particles **100**) may be chosen from, for example, activated carbon, alumina and other metal oxides, clay, hopcalite, ion exchange resins, molecular sieves and zeolites, silica, sodium bicarbonate, and so on including combinations of any of these materials. In particular embodiments, secondary sorbent particles (e.g. activated carbon) may be impregnated sorbent particles that are suitably impregnated with e.g. any desired metal salt or compound. Various particles (including impregnated particles) that may be suitable for use as secondary sorbent particles are described in detail in U. S. Patent Application Publication No. 2015/0306536 to Billingsley, which is incorporated by reference in its entirety herein for this purpose. Any combination of any of these particles may be used.

In some embodiments, an air filter **1** comprising sorbent particles **100** as disclosed herein, may be used in combination with a secondary air filter that is provided separately from air filter **1**. In some embodiments, an air filter **1** and a secondary air filter may be separately installed into different areas of an air-handling apparatus. (For example, an air filter **1** and a secondary air filter may each be a framed air filter and may each be separately inserted e.g. into a room air purifier.) Alternatively, an air filter **1** and a secondary air filter may be assembled together (and e.g. attached to each other) before being installed into e.g. an air-handling apparatus. Air filter **1** can be placed e.g. upstream or downstream of the secondary air filter (if air filter **1** is upstream, it may serve e.g. as a prefilter for the secondary filter). In some exemplary embodiments, a secondary air filter may be configured e.g. to capture fine particles, and may exhibit a Percent Penetration of e.g. less than about 80, 70, 60, 50, 40, 30, 20, 10, or 5.

A filter support **10** comprising sorbent particles **100** as disclosed herein may be used in any kind of air filter **1**, configured for any suitable end use. By way of specific examples, filter support **10** may find use in e.g. an air filter that is, or is part of, a personal respiratory protection device. It has already been noted that filter support **10** may take the form of a filter cartridge that can be fluidly coupled to a mask body to provide a personal respiratory protection device (e.g., the filter cartridge being disposable and the mask body being a piece that is shaped to fit a user's face and that is retained and a replacement filter cartridge attached thereto at an appropriate time). In other embodiments, filter support **10** may be incorporated into a "filtering face-piece" respirator mask **60**. In products of this general type, the mask body itself provides the filtering function. That is, unlike respirators that use mask bodies in conjunction with attachable filter cartridges or the like, filtering face-piece respirators are designed to have the filtration layer(s) present over much or essentially all of the entire mask body so that there is no need for installing or replacing a filter cartridge. (That is, in a filtering face-piece respirator the mask body itself performs the filtering function rather than relying on one or more cartridges attached thereto.) Filtering face-piece respirators **60** often come in one of two configurations: molded (e.g. shaped, into a generally cup-shape so as to fit on a user's face) as shown in exemplary representation in FIG. **6**, and flat-fold, that can be supplied in a flat or nearly-flat condition and can then be unfolded and expanded to fit on a user's face, as shown in exemplary representation in FIG. **7**.

Such a respirator mask (whether e.g. a flat-fold or molded respirator) **60** may comprise any desired ancillary layers (e.g., one or more cover layers, stiffening layers, pre-filter layers, and the like) and components (e.g. one or more exhaust valves, attachment bands or strings, nose-pieces, and so on). If used in a flat-fold respirator mask, filter support **10** may often take the form of a relatively flexible layer (e.g. with one or more preferential folding lines **63** provided to make the material more easily foldable). If filter support **10** is to be used in a molded respirator mask (that is not designed to be foldable), filter support **10** may be e.g. a somewhat semi-rigid material (noting however that since in many molded, cup-shaped respirator masks much of the stiffness may be provided by a stiffening layer that is separate from the filtering layer(s), it may not be strictly necessary that filter support **10** be rigid, or even semi-rigid, for use in such a product).

It will be appreciated that the above-described uses fall primarily into the category of so-called "negative-pressure" respirators; that is, products in which the motive power for moving air is the breathing of a user rather than a separately provided motorized fan. Such negative-pressure respirators are often configured as e.g. full-face respirators, half-face respirators, and hoods (e.g., escape hoods, smoke hoods, and the like). All such products are encompassed by the term negative-pressure respirator as used herein, and filter support **10** may be used with any such product.

In other embodiments, filter support **10** may be used in a respirator in which the motive power for moving air is a motorized fan or blower. Such products may include e.g. a PAPR (powered air purifying respirator). In such products, filter support **10** (and, in general, air filter **1**) may be located proximate the user's face or head; or, it may be located remotely (e.g., positioned in a receptacle of a belt-worn housing).

In some embodiments as shown in exemplary embodiment in FIG. **8**, a filter support **10** (e.g., whether pleated or not, and whether or not including any other layers such as

particle-filtration layers, etc.) may be incorporated into an air filter **1** that includes a perimeter frame **70** (e.g. a rigidifying or supporting frame), which may be e.g. arranged around a perimeter edge region of the filter support. Suitable materials for the frame include chip board, or paperboard, synthetic plastic materials and metal. Suitable frame constructions might be chosen from e.g. the "pinch" frame construction illustrated in FIGS. 1-4 of U.S. Pat. No. 6,126,707 to Pitzen, the "box" frame construction illustrated in FIGS. 5 and 6 of the '707 Patent, the hybrid frame construction illustrated in FIGS. 7-11 of the '707 Patent, any of the frame constructions disclosed in U.S. Pat. No. 7,503,953 to Sundet, and any of the frame constructions disclosed in U.S. Pat. No. 7,235,115 to Duffy. Any such frame may be attached to the filter support by any suitable method, e.g. hot-melt bonding, room-temperature glue, and so on.

An air filter **1** (whether framed or not) comprising filter support **10** may be advantageously used to filter moving air in any suitable powered air-handling system, e.g. in HVAC systems (e.g., in forced-air heating, cooling, and/or heating/cooling systems often used in residences, office buildings, retail establishments, and so on). Such filters may also find use in room air purifiers, motor vehicles (such as in e.g. cabin air filtration of automobiles), clean rooms, operating rooms, and the like. In some embodiments, air filter **1** (e.g., as part of a filter cartridge) may be inserted into an air pathway of a powered air-purifying respirator, as noted above. While in any or all such uses it may not be necessary that air filter **1** be a framed air filter, in many such uses it may be advantageous for air filter **1** to be a framed air filter.

The above discussions relate to methods of providing polymeric sorbent particles **100** on a suitable filter support **10** to provide an air filter **1** and positioning the air filter so that the supported sorbent particles are exposed to air (the term air is used broadly and encompasses any gas or gaseous mixture, e.g. nitrogen, dehumidified nitrogen or air, oxygen-enriched air, air including an anesthetic gas or gas mixture, and so on). In many embodiments, the air to which the sorbent particles are exposed is in the form of a moving airstream. In some cases (which may be referred to as "active" filtration) such moving air may be motivated by a motorized blower, fan, and so on. In other cases (which may be referred to as "passive" filtration) such moving air may be motivated e.g. by the breathing of a person rather than by any motorized mechanism. The term "passive" filtration also encompasses situations in which an air filter **1** is exposed to currents, eddies, and the like, e.g. in an ambient atmosphere. Such currents and eddies might take the form of e.g. wind (such as might be impinged against an exterior surface of a filter support **10** that is provided in the form of e.g. a window screen). Or, in indoor environments, such currents and eddies might take the form of convection currents, random air currents, and the like, which regularly occur e.g. in rooms of buildings (due e.g. to doors opening and closing, persons moving, and so on). It will thus be appreciated that an air filter **1** as disclosed herein encompasses such devices as e.g. a cartridge, bag, pouch, canister, or, in general, any kind of container that holds sorbent particles **100** therein and that has at least one air-permeable wall so as to allow air to enter the container and contact the sorbent particles and to then exit the container, regardless of whether such a device is or is not used with any kind of mechanical blower or is used in any kind of respirator.

In broad summary, air filters **1** as described herein can find use in any suitable application in which it is desired to remove at least some aldehyde molecules from air. Such uses may involve personal devices (e.g. personal respiratory

protection devices) designed for use by a single user, or collective devices (e.g. room air purifiers, HVAC systems, and so on) designed for e.g. buildings, vehicles, and other places where persons reside, work, or gather. As noted, such uses may involve “active” or “passive” filtration, and may use an air filter **1** that is configured in any of a wide variety of geometric formats and that is comprised of any of a wide variety of materials. Also as noted, one or more secondary sorbents may be used in addition to the herein-described polymeric sorbent particles **100**, whether mixed with particles **100** and/or provided in a separate layer. As further noted, an air filter **1** may include at least one layer (in addition to the at least one support layer **10** that supports polymeric sorbent particles **100**) that provides fine-particle filtration and/or that captures some gas/vapor other than aldehydes. Instead of this, or as an adjunct to this, a secondary air filter may be provided in addition to air filter **1**, e.g. to perform filtration of fine particles and/or to capture some other gas/vapor. Moreover, combinations of any of the above-described embodiments of filter supports may be used. For example, polymeric sorbent particles **100** might be disposed within a fibrous web, or onto a surface of a netting, which web or netting might e.g. be placed within a housing to provide a filter cartridge.

The polymeric sorbent particles **100** are a reaction product of a hydrolyzed divinylbenzene/maleic anhydride polymeric material having carboxylic acid groups (—COOH groups) with a nitrogen-containing compound having two primary and/or secondary amino groups. The nitrogen-containing compound has a first primary and/or secondary amino group that is ionically attached to the hydrolyzed divinylbenzene/maleic anhydride polymeric material in the polymeric sorbent. Further, the nitrogen-containing compound has at least one second primary amino group and/or secondary amino group that can react with an aldehyde.

The polymeric sorbent can be used to sorb aldehydes that are volatile at room temperature or under use conditions. Suitable aldehydes are typically of Formula (I)



where  $R_2$  is hydrogen, alkyl, vinyl, or aryl. The molecular weight of the aldehyde of Formula (I) is typically no greater than 200 grams/mole. In some embodiments, the aldehyde is formaldehyde ( $R_2$  is hydrogen) or acetaldehyde ( $R_2$  is methyl).

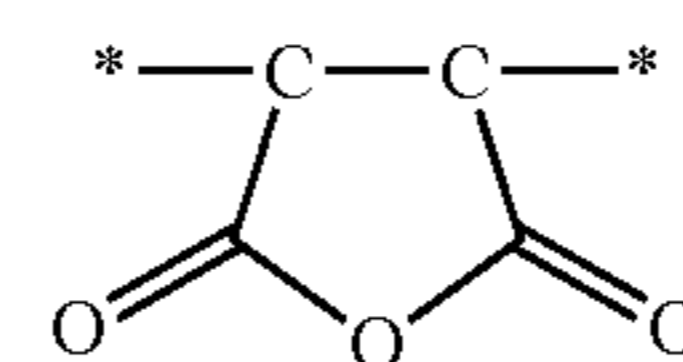
The term “porous” when referring to a polymeric material means that the polymeric material has pores and can sorb gaseous substances such as, for example, aldehydes. In most embodiments, the polymeric sorbent is porous. Porous materials such as the polymeric sorbents can be characterized based on the size of their pores. The term “micropores” refers to pores having a diameter less than 2 nanometers. The term “mesopores” refers to pores having a diameter in a range of 2 to 50 nanometers. The term “macropores” refers to pores having a diameter greater than 50 nanometers. The porosity of a polymeric material can be characterized from an adsorption isotherm of an inert gas such as nitrogen or argon by the polymeric material under cryogenic conditions (e.g., liquid nitrogen at 77 K). The adsorption isotherm is typically obtained by measuring adsorption of the inert gas such as nitrogen or argon by the polymeric material at multiple relative pressures ( $p/p^0$ ) in a range of about  $10^{-6}$  to about  $0.98+0.01$ . The isotherms are then analyzed using various methods such as the BET (Brunauer-Emmett-Teller) method to calculate specific surface area and the Density Functional Theory (DFT) to characterize the porosity and the pore size distribution.

As noted, the polymeric sorbent is formed by reacting a hydrolyzed divinylbenzene/maleic anhydride polymeric material having carboxylic acid groups and a nitrogen-containing compound having at least two amino groups of formula —NHR where R is hydrogen or alkyl. One of the at least two amino groups forms an ionic bond with carboxylic acid groups in the hydrolyzed divinylbenzene/maleic anhydride polymeric material. That is, the nitrogen-containing compound becomes part of the polymeric sorbent.

The hydrolyzed divinylbenzene/maleic anhydride polymeric material is formed from a divinylbenzene/maleic anhydride precursor polymeric material. The conditions used to synthesize the precursor polymeric material are typically selected so that this material has a BET specific surface area equal to at least  $100 \text{ m}^2/\text{gram}$ .

The precursor polymeric material (i.e., the divinylbenzene/maleic anhydride precursor polymeric material) is typically synthesized from a polymerizable composition that includes a monomer mixture containing maleic anhydride, divinylbenzene, and an optional styrene-type monomer. The precursor polymeric material is usually formed from a monomer mixture containing 1) 8 to 65 weight percent maleic anhydride, 2) 30 to 85 weight percent divinylbenzene, and 3) 0 to 40 weight percent of a styrene-type monomer, wherein the styrene-type monomer is styrene, an alkyl-substituted styrene, or a combination thereof. The amounts are based on the total weight of monomers in the monomer mixture, which is equal to the total weight of monomers in the polymerizable composition. When the precursor polymeric material is used to form a polymeric sorbent that is particularly effective for sorption of aldehydes, the monomer mixture often contains 1) 15 to 65 weight percent maleic anhydride, 2) 30 to 85 weight percent divinylbenzene, and 3) 0 to 40 weight percent of a styrene-type monomer, wherein the styrene-type monomer is styrene, an alkyl-substituted styrene, or a combination thereof.

The maleic anhydride that is included in the monomer mixture results in the formation of maleic anhydride monomeric units of Formula (II) within the precursor polymeric material.



(II)

The asterisks in this formula and other formulas contained herein denote the location of attachment of the monomeric unit to another monomeric unit or to a terminal group.

The amount of maleic anhydride used to form the precursor polymeric material influences the amount of nitrogen-containing compound that can react with the precursor polymeric material to form the polymeric sorbent. The nitrogen-containing compound reacts with the anhydride group to become ionically attached to the polymeric material that is the polymeric sorbent.

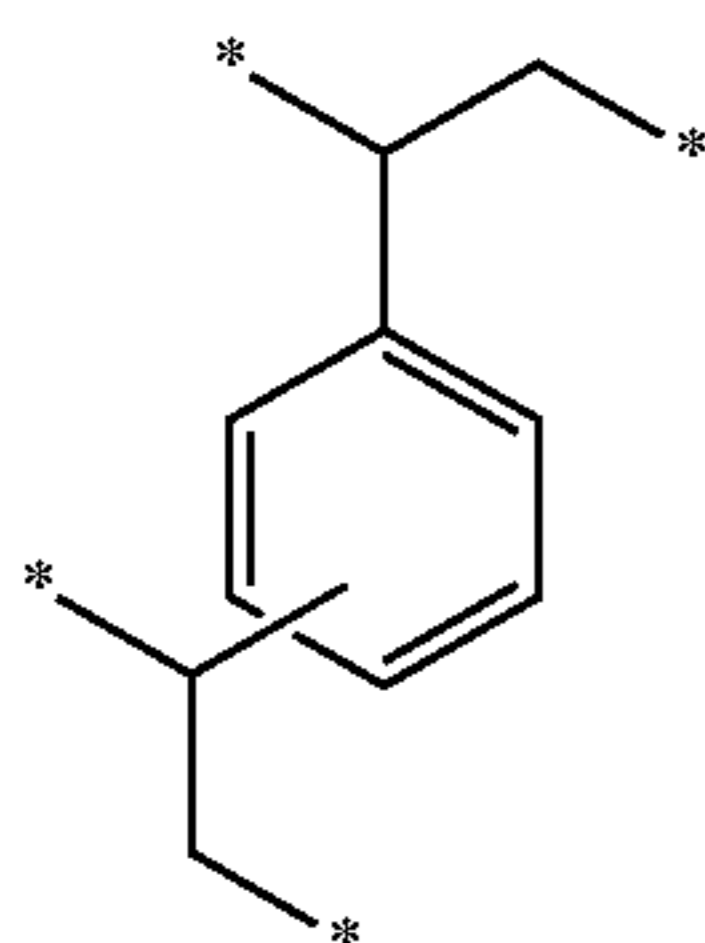
In some embodiments, the amount of maleic anhydride included in the monomer mixture is at least 8 weight percent, at least 10 weight percent, at least 12 weight percent, at least 15 weight percent, or at least 20 weight percent. The amount of maleic anhydride can be up to 65 weight percent, up to 60 weight percent, up to 55 weight percent, up to 50 weight percent, up to 45 weight percent, up to 40 weight percent, up to 35 weight percent, up to 30 weight percent, or up to 25 weight percent. For example, the

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maleic anhydride may be present in a range of 8 to 65 weight percent, 15 to 65 weight percent, 15 to 60 weight percent, 15 to 50 weight percent, 15 to 40 weight percent, 20 to 65 weight percent, 20 to 60 weight percent, 20 to 50 weight percent, 20 to 40 weight percent, 30 to 65 weight percent, 30 to 60 weight percent, 30 to 50 weight percent, 40 to 65 weight percent, or 40 to 60 weight percent. The amounts are based on the total weight of monomers in the monomer mixture contained in the polymerizable composition used to form the precursor polymeric material.

Stated differently, the precursor polymeric material contains monomeric units of Formula (II) in a range of 8 to 65 weight percent, 15 to 65 weight percent, 15 to 60 weight percent, 15 to 50 weight percent, 15 to 40 weight percent, 20 to 65 weight percent, 20 to 60 weight percent, 20 to 50 weight percent, 20 to 40 weight percent, 30 to 65 weight percent, 30 to 60 weight percent, 30 to 50 weight percent, 40 to 65 weight percent, or 40 to 60 weight percent. These amounts are based on the total weight of the monomeric units in the precursor polymeric material.

The divinylbenzene included in the monomer mixture results in the formation of divinylbenzene monomeric units of Formula (III) within the precursor polymeric material.



(III)

The two groups attached to the benzene ring can be in an ortho, meta, or para arrangement to each other. The monomeric units of Formula (III) contribute to the high crosslink density and to the formation of a rigid polymeric material having micropores and/or mesopores.

The amount of divinylbenzene used to form the precursor polymeric material can have a strong influence on the BET specific surface area of both the precursor polymeric material and the polymeric sorbent. The BET specific surface area tends to increase with an increase in the amount of divinylbenzene in the monomer mixture used to form the precursor polymeric material and with the resulting amount of monomeric units of Formula (III) in the polymeric sorbent. If the amount of divinylbenzene is less than 30 weight percent, the polymeric sorbent may not have a sufficiently high BET specific surface area. On the other hand, if the amount of divinylbenzene is greater than 85 weight percent, the amount of aldehyde sorbed may be compromised because there are fewer nitrogen-containing groups in the polymeric sorbent. In some embodiments, the amount of divinylbenzene included in the monomer mixture is at least 30 weight percent, at least 35 weight percent, at least 40 weight percent, or at least 45 weight percent. The amount of divinylbenzene can be up to 85 weight percent, up to 80 weight percent, up to 75 weight percent, up to 70 weight percent, up to 65 weight percent, up to 60 weight percent, or up to 50 weight percent. For example, the amount can be in a range of 30 to 85 weight percent, 30 to 80 weight percent, 30 to 75 weight percent, 30 to 70 weight percent, 30 to 65 weight percent, 30 to 60 weight percent, 30 to 55 weight percent, 30 to 50 weight percent, 35 to 80 weight

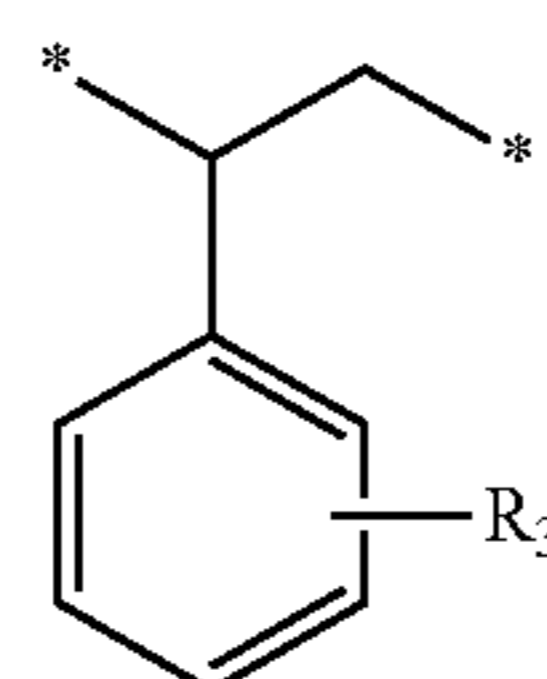
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percent, 35 to 70 weight percent, 35 to 60 weight percent, 40 to 85 weight percent, 40 to 80 weight percent, 40 to 70 weight percent, or 40 to 60 weight percent. The amounts are based on the total weight of monomers in the monomer mixture contained in the polymerizable composition used to form the precursor polymeric material.

Stated differently, the precursor polymeric material contains monomeric units of Formula (III) in a range of 30 to 85 weight percent, 30 to 80 weight percent, 30 to 75 weight percent, 30 to 70 weight percent, 30 to 65 weight percent, 30 to 60 weight percent, 30 to 55 weight percent, 30 to 50 weight percent, 35 to 80 weight percent, 35 to 70 weight percent, 35 to 60 weight percent, 40 to 85 weight percent, 40 to 80 weight percent, 40 to 70 weight percent, or 40 to 60 weight percent. These amounts are based on the total weight of the monomeric units in the precursor polymeric material.

Divinylbenzene can be difficult to obtain in a pure form. For example, divinylbenzene is often commercially available with purity as low as 55 weight percent. Obtaining divinylbenzene with purity greater than about 80 weight percent can be difficult and/or expensive. The impurities accompanying divinylbenzene are typically styrene-type monomers such as styrene, alkyl-substituted styrene (e.g., ethyl styrene), or mixtures thereof. Thus, styrene-type monomers are often present along with divinylbenzene and maleic anhydride in the monomer mixture contained in the polymerizable composition used to form the precursor polymeric material. The monomer mixture typically contains 0 to 40 weight percent styrene-type monomers based on the total weight of monomers in the monomer mixture. If the content of the styrene-type monomer is greater than 40 weight percent, the crosslink density may be too low and/or the distance between crosslinks may be too large to provide a divinylbenzene/maleic anhydride precursor polymeric material having a BET specific surface area equal to at least 100 m<sup>2</sup>/gram. As the crosslink density decreases, the polymeric sorbent tends to be less rigid and less porous. Typically, divinylbenzene having a purity of 55 weight percent is not suitable for use in the monomer mixtures used to form the precursor polymeric material because the content of styrene-type monomer impurities is too high. If the monomer mixture contains too much styrene-type monomer, the amount of divinylbenzene may be undesirably low. Using divinylbenzene having a lower purity than about 80 weight percent can result in the formation of a precursor polymeric material and/or a polymeric sorbent with an undesirably low BET specific surface area.

The styrene-type monomers included in the monomer mixture result in the presence of styrene-type monomeric units of Formula (IV) within the precursor polymeric material.



(IV)

Group R<sub>3</sub> is hydrogen or alkyl (e.g., an alkyl having 1 to 10 carbon atoms, 1 to 6 carbon atoms or 1 to 4 carbon atoms).

In some embodiments, the amount of styrene-type monomers used to form the precursor polymeric material, is at least 1 weight percent, at least 2 weight percent, or at least



5 weight percent. The amount of styrene-type monomers can be up to 40 weight percent, up to 30 weight percent, up to 20 weight percent, or up to 10 weight percent. For example, the amount can be in a range of 0 to 40 weight percent, 1 to 40 weight percent, 5 to 40 weight percent, 10 to 40 weight percent, 0 to 30 weight percent, 1 to 30 weight percent, 5 to 30 weight percent, 10 to 30 weight percent, 0 to 20 weight percent, 1 to 20 weight percent, 5 to 20 weight percent, or 10 to 20 weight percent. The amounts are based on the total weight of monomers in the monomer mixture contained in the polymerizable composition used to form the precursor polymeric material.

Stated differently, the precursor polymeric material contains monomeric units of Formula (IV) in a range of 0 to 40 weight percent, 1 to 40 weight percent, 5 to 40 weight percent, 10 to 40 weight percent, 0 to 30 weight percent, 1 to 30 weight percent, 5 to 30 weight percent, 10 to 30 weight percent, 0 to 20 weight percent, 1 to 20 weight percent, 5 to 20 weight percent, or 10 to 20 weight percent. These amounts are based on the total weight of the monomeric units in the precursor polymeric material.

Overall, the precursor polymeric material is formed from a polymerizable composition containing a monomer mixture that includes 8 to 65 weight percent maleic anhydride, 30 to 85 weight percent divinylbenzene, and 0 to 40 weight percent of a styrene-type monomer. In some embodiments, the monomer mixture contains 15 to 65 weight percent maleic anhydride, 30 to 85 weight percent divinylbenzene, and 0 to 40 weight percent (or 5 to 40 weight percent) of a styrene-type monomer. Some embodiments contain 25 to 65 weight percent maleic anhydride, 30 to 75 weight percent divinylbenzene, and 1 to 20 weight percent (or 5 to 20 weight percent) styrene-type monomer. Some embodiments contain 25 to 60 weight percent maleic anhydride, 30 to 75 weight percent divinylbenzene, and 1 to 30 weight percent (or 5 to 30 weight percent or 10 to 30 weight percent) styrene-type monomer. In still other embodiments, the monomer mixture contains 30 to 65 weight percent maleic anhydride, 30 to 70 weight percent divinylbenzene, and 1 to 20 weight percent (or 5 to 20 weight percent or 10 to 20 weight percent) styrene-type monomer. In still other embodiments, the monomer mixture contains 30 to 60 weight percent maleic anhydride, 30 to 65 weight percent divinylbenzene, and 1 to 20 weight percent (or 5 to 20 weight percent or 10 to 20 weight percent) styrene-type monomer. In further embodiments, the monomer mixture contains 40 to 60 weight percent maleic anhydride, 30 to 55 weight percent divinylbenzene, and 1 to 20 weight percent (or 5 to 20 weight percent, or 10 to 20 weight percent) styrene-type monomers. In still further embodiments, the monomer mixture contains 20 to 40 weight percent maleic anhydride, 50 to 70 weight percent divinylbenzene, and 1 to 20 weight percent (or 5 to 20 weight percent or 10 to 20 weight percent) styrene-type monomer. The weight percent values are based on the total weight of monomers in the monomer mixture used to form the precursor polymeric material.

The monomer mixture included in the polymerizable composition used to form the precursor polymeric material typically contains at least 95 weight percent monomers selected from maleic anhydride, divinylbenzene, and styrene-type monomer. For example, at least 97 weight percent, at least 98 weight percent, at least 99 weight percent, at least 99.5 weight percent, at least 99.9 weight percent, or 100 weight percent of the monomers in the monomer mixture are selected from maleic anhydride, divinylbenzene, and styrene-type monomer. In some embodiments, where high

purity divinylbenzene is used, the monomer mixture contains only divinylbenzene and maleic anhydride. That is, the sum of the amount of divinylbenzene and maleic anhydride is 100 weight percent.

In addition to the monomer mixture, the polymerizable composition used to form the precursor polymeric material includes an organic solvent. The polymerizable composition is a single phase prior to polymerization. Stated differently, prior to polymerization, the polymerizable composition is not a suspension. The organic solvent is selected to dissolve the monomers included in the monomer mixture and to solubilize the precursor polymeric material as it begins to form. The organic solvent typically includes a ketone, ester, acetonitrile, or mixture thereof.

The organic solvent can function as a porogen during the formation of the precursor polymeric material. The organic solvent choice can strongly influence the BET specific surface area and the size of the pores formed in the precursor polymeric material. Using organic solvents that are miscible with both the monomers and the forming polymer tends to result in the formation of micropores and mesopores within the precursor polymeric material. Good solvents for the monomers and the forming polymer tend to result in a larger fraction of the porosity of the precursor polymeric material being in the form of micropores and mesopores.

Organic solvents that are particularly suitable for producing precursor polymeric materials with micropores and mesopores include ketones, esters, acetonitrile, and mixtures thereof. The organic solvent can affect the BET specific surface area of the precursor polymeric material. Typically, it is desirable that the precursor polymeric material has a BET surface area equal to at least 100 m<sup>2</sup>/gram. Provided that the resulting precursor polymeric material has a BET specific surface area equal to at least 100 m<sup>2</sup>/gram, other organic solvents can be added along with one or more of the organic solvents listed above. Examples of suitable ketones include, but are not limited to, alkyl ketones such as methyl ethyl ketone and methyl isobutyl ketone. Examples of suitable esters include, but are not limited to, acetate esters such as ethyl acetate, propyl acetate, butyl acetate, amyl acetate, and tert-butyl acetate.

The organic solvent can be used in any desired amount. The polymerizable compositions often have percent solids in a range of 1 to 75 weight percent (i.e., the polymerizable composition contains 25 to 99 weight percent organic solvent). If the percent solids are too low, the polymerization time may become undesirably long. The percent solids are often at least 1 weight percent, at least 2 weight percent, at least 5 weight percent, at least 10 weight percent, or at least 15 weight percent. If the weight percent solids is too great, however, the monomers do not form a single phase with the organic solvent. Further, increasing the percent solids tends to result in the formation of precursor polymeric material with a lower BET specific surface area. The percent solids usually can be up to 75 weight percent, up to 70 weight percent, up to 60 weight percent, up to 50 weight percent, up to 40 weight percent, up to 30 weight percent, or up to 25 weight percent. For example, the percent solids can be in a range of 5 to 75 weight percent, 5 to 70 weight percent, 5 to 60 weight percent, 5 to 50 weight percent, 5 to 40 weight percent, 5 to 30 weight percent, or 5 to 25 weight percent.

In addition to the monomer mixture and organic solvent, the polymerizable compositions used to form the precursor polymeric material typically include an initiator for free radical polymerization reactions. Any suitable free radical initiator can be used. Suitable free radical initiators are typically selected to be miscible with the monomers

included in the polymerizable composition. In some embodiments, the free radical initiator is a thermal initiator that can be activated at a temperature above room temperature. In other embodiments, the free radical initiator is a redox initiator. Because the polymerization reaction is a free radical reaction, it is desirable to minimize the amount of oxygen in the polymerizable composition.

Both the type and amount of initiator can affect the polymerization rate. In general, increasing the amount of the initiator tends to lower the BET specific surface area; however, if the amount of initiator is too low, it may be difficult to obtain high conversions of the monomers to polymeric material. The free radical initiator is typically present in an amount in a range of 0.05 to 10 weight percent, 0.05 to 8 weight percent, 0.05 to 5 weight percent, 0.1 to 10 weight percent, 0.1 to 8 weight percent, 0.1 to 5 weight percent, 0.5 to 10 weight percent, 0.5 to 8 weight percent, 0.5 to 5 weight percent, 1 to 10 weight percent, 1 to 8 weight percent, or 1 to 5 weight percent. The weight percent is based on the total weight of monomers in the polymerizable composition.

Suitable thermal initiators include organic peroxides and azo compounds. Example azo compounds include, but are not limited to, those commercially available under the trade designation VAZO from E.I. du Pont de Nemours Co. (Wilmington, Del.) such as VAZO 64 (2,2'-azobis(isobutyronitrile)), which is often referred to as AIBN, and VAZO 52 (2,2'-azobis(2,4-dimethylpentanenitrile)). Other azo compounds are commercially available from Wako Chemicals USA, Inc. (Richmond, Va.) such as V-601 (dimethyl 2,2'-azobis(2-methylproprionate)), V-65 (2,2'-azobis(2,4-dimethyl valeronitrile)), and V-59 (2,2'-azobis(2-methylbutyronitrile)). Organic peroxides include, but are not limited to, bis(1-oxoaryl)peroxides such as benzoyl peroxide (BPO), bis(1-oxoalkyl)peroxides such as lauroyl peroxide, and dialkyl peroxides such as dicumyl peroxide or di-tert-butyl peroxide and mixtures thereof. The temperature needed to activate the thermal initiator is often in a range of 25° C. to 160° C., in a range of 30° C. to 150° C., in a range of 40° C. to 150° C., in a range of 50° C. to 150° C., in a range of 50° C. to 120° C., or in a range of 50° C. to 110° C.

Suitable redox initiators include arylsulfinate salts, triarylsulfonium salts, or N,N-dialkylaniline (e.g., N,N-dimethylaniline) in combination with a metal in an oxidized state, a peroxide, or a persulfate. Specific arylsulfinate salts include tetraalkylammonium arylsulfonates such as tetrabutylammonium 4-ethoxycarbonylbenzenesulfinate, tetrabutylammonium 4-trifluoromethylbenzenesulfinate, and tetrabutylammonium 3-trifluoromethylbenzenesulfinate. Specific triarylsulfonium salts include those with a triphenylsulfonium cation and with an anion selected from  $\text{PF}_6^-$ ,  $\text{AsF}_6^-$ , and  $\text{SbF}_6^-$ . Suitable metal ions include, for example, ions of group III metals, transition metals, and lanthanide metals. Specific metal ions include, but are not limited to, Fe(III), Co(III), Ag(I), Ag(II), Cu(II), Ce(III), Al (III), Mo(VI), and Zn(II). Suitable peroxides include benzoyl peroxide, lauroyl peroxide, and the like. Suitable persulfates include, for example, ammonium persulfate, tetraalkylammonium persulfate (e.g., tetrabutylammonium persulfate), and the like.

The polymerizable composition is typically free or substantially free of surfactants. As used herein, the term "substantially free" in reference to the surfactant means that no surfactant is purposefully added to the polymerizable composition and any surfactant that may be present is the result of being an impurity in one of the components of the polymerizable composition (e.g., an impurity in the organic

solvent or in one of the monomers). The polymerizable composition typically contains less than 0.5 weight percent, less than 0.3 weight percent, less than 0.2 weight percent, less than 0.1 weight percent, less than 0.05 weight percent, or less than 0.01 weight percent surfactant based on the total weight of the polymerizable composition. The absence of a surfactant is advantageous because these materials tend to restrict access to and, in some cases, fill micropores and mesopores in a precursor polymeric material.

When the polymerizable composition is heated in the presence of a free radical initiator, polymerization of the monomers in the monomer mixture occurs. By balancing the amounts of each monomer in the monomer mixture and by selection of an organic solvent that can solubilize all of the monomers and the growing polymeric material during its early formation stage, a precursor polymeric material can be prepared that has a BET specific surface area equal to at least 100 m<sup>2</sup>/gram. The BET specific surface area of the precursor polymeric material can be at least 150 m<sup>2</sup>/gram, at least 200 m<sup>2</sup>/gram, or at least 300 m<sup>2</sup>/gram. The BET specific surface area can be, for example, up to 1000 m<sup>2</sup>/gram or higher, up to 900 m<sup>2</sup>/gram, up to 800 m<sup>2</sup>/gram, up to 750 m<sup>2</sup>/gram, or up to 700 m<sup>2</sup>/gram.

The structure of the divinylbenzene/maleic anhydride polymeric material is particularly well suited for use as a precursor polymeric material for the porous polymeric sorbent. Providing that the content of monomeric units of Formula (IV) from styrene-type monomers is low, the divinylbenzene/maleic anhydride precursor polymeric material has alternating monomeric units from divinylbenzene and maleic anhydride. This structure results in high crosslinking and contributes to the formation of a porous polymeric material, particularly a porous polymeric material having a high content of micropores and/or mesopores.

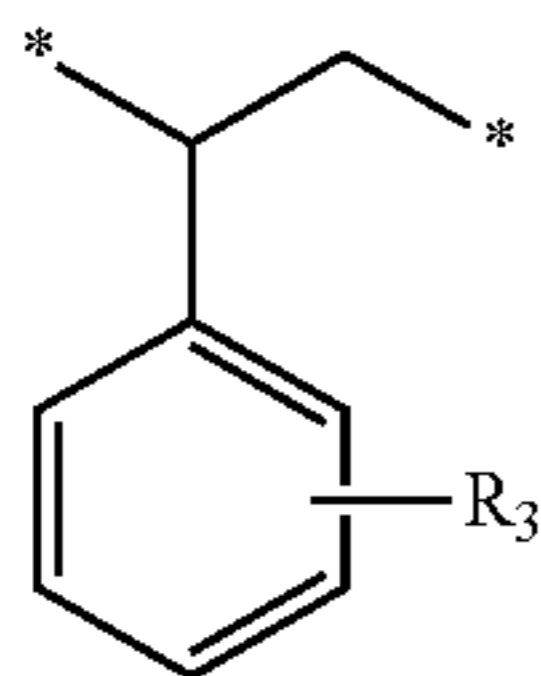
The precursor polymeric material is the reaction product of the polymerizable composition. The precursor polymeric material is usually formed from the polymerizable composition that contains (a) 8 to 65 weight percent of a first monomeric unit of Formula (II),



(b) 30 to 85 weight percent of a second monomeric unit of Formula (III), and



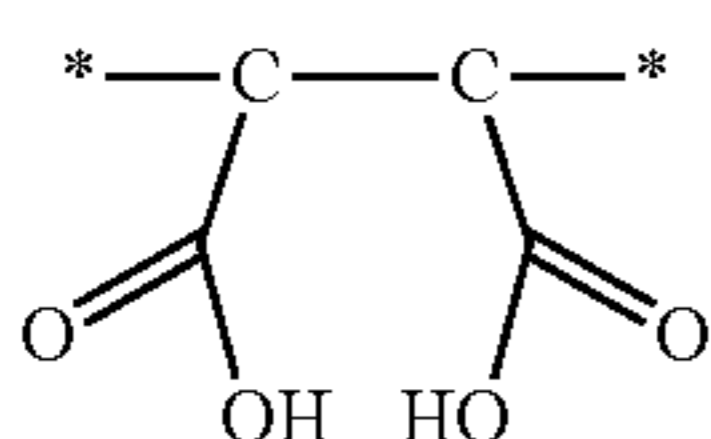
(c) 0 to 40 weight percent of a third monomeric unit of Formula (IV) wherein R<sub>3</sub> is hydrogen or alkyl (e.g., an alkyl having 1 to 10 carbon atoms, 1 to 6 carbon atoms, or 1 to 4 carbon atoms).



In many embodiments, to be particularly effective as a polymeric sorbent for aldehydes, the precursor polymeric material contains (a) 15 to 65 weight percent of a first monomeric unit of Formula (II), (b) 30 to 85 weight percent of a second monomeric unit of Formula (III), and (c) 0 to 40 weight percent (or 5 to 40 weight percent) of a third monomeric unit of Formula (IV). Each weight percent value is based on the total weight of monomeric units in the precursor polymeric material.

Some embodiments of the precursor polymeric material contain 25 to 65 weight percent of the first monomeric unit of Formula (II), 30 to 75 weight percent of the second monomeric unit of Formula (III), and 1 to 20 weight percent (or 5 to 20 weight percent) of the third monomeric unit of Formula (IV). Some embodiments contain 25 to 60 weight percent of the first monomeric unit of Formula (II), 30 to 75 weight percent of the second monomeric unit of Formula (III), and 1 to 30 weight percent (or 5 to 30 weight percent or 10 to 30 weight percent) of the third monomeric unit of Formula (IV). In still other embodiments, the monomer mixture contains 30 to 65 weight percent of the first monomeric unit of Formula (II), 30 to 70 weight percent of the second monomeric unit of Formula (III), and 1 to 20 weight percent (or 5 to 20 weight percent or 10 to 20 weight percent) of the third monomeric unit of Formula (IV). In still other embodiments, the monomer mixture contains 30 to 60 weight percent of the first monomeric unit of Formula (II), 30 to 65 weight percent of the second monomeric unit of Formula (III), and 1 to 20 weight percent (or 5 to 20 weight percent or 10 to 20 weight percent) of the third monomeric unit of Formula (IV). In further embodiments, the monomer mixture contains 40 to 60 weight percent of the first monomeric unit of Formula (II), 30 to 55 weight percent of the second monomeric unit of Formula (III), and 1 to 20 weight percent (or 5 to 20 weight percent, or 10 to 20 weight percent) of the third monomeric unit of Formula (IV). In still further embodiments, the monomer mixture contains 20 to 40 weight percent of the first monomeric unit of Formula (II), 50 to 70 weight percent of the second monomeric unit of Formula (III), and 1 to 20 weight percent (or 5 to 20 weight percent or 10 to 20 weight percent) of the third monomeric unit of Formula (IV). The weight percent values are based on the total weight of monomeric units used in the precursor polymeric material.

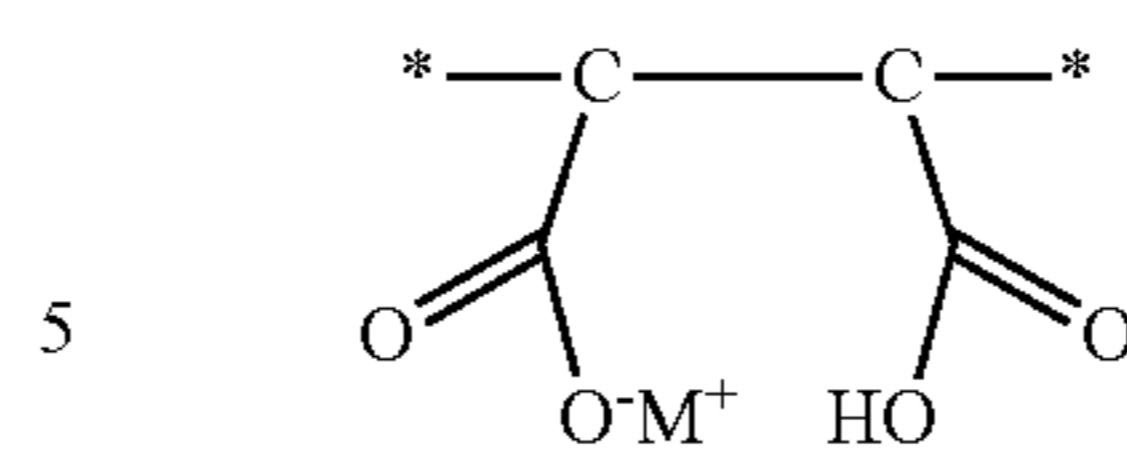
The precursor polymeric material is hydrolyzed to form a hydrolyzed divinylbenzene/maleic anhydride polymeric material. Hydrolysis results in the ring opening of the groups of Formula (II) in the precursor polymeric material. That is, the hydrolyzed divinylbenzene/maleic anhydride polymeric material includes one or more of the following types of groups (VII-A, VII-B, and VII-C) depending on the pH conditions and the particular hydrolyzing agent selected.



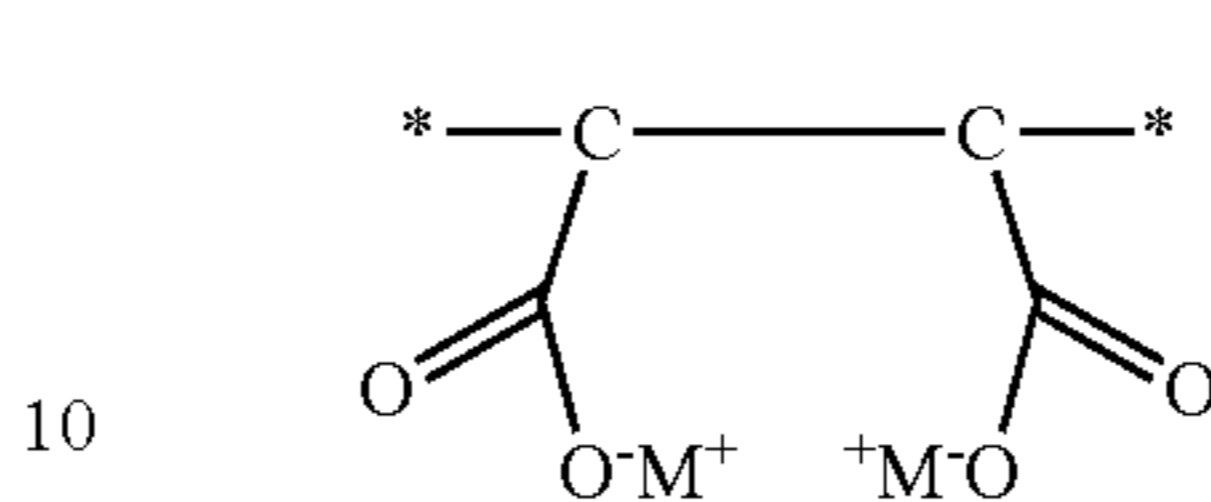
(VII-A)

-continued

(IV)



(VII-B)



(VII-C)

10

15

20

25

30

35

40

45

50

55

60

65

Groups of Formula (VII-A) have two carboxylic acid groups. Groups of Formula (VII-B) have both a carboxylic acid group and a carboxylate anion. Groups of Formula (VII-C) have two carboxylate anions. In groups of Formulas (VII-B) and (VII-C),  $M^+$  can be any suitable cation but is often an alkaline metal cation such as sodium or potassium. The hydrolysis reaction typically converts at least 70 mole percent, at least 75 mole percent, at least 80 mole percent, at least 85 mole percent, at least 90 mole percent, at least 95 mole percent, at least 97 mole percent, at least 98 mole percent, at least 99 mole percent, or 100 mole percent of the anhydride groups to carboxylic acid and/or carboxylate groups.

The hydrolysis reaction is often performed at room temperature or close to room temperature by mixing the precursor polymeric material with a solution of an alkaline metal hydroxide, alkaline metal carbonate, alkaline metal bicarbonate, or combination thereof. Specific examples include, but are not limited to sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium carbonate, sodium bicarbonate, or mixtures thereof. The solutions are typically water-based, alcohol-based, or both.

Alternatively, the hydrolysis reaction may occur by simply heating the precursor polymer at an elevated temperature (e.g., 25 to 120° C.) in water.

After hydrolysis, the hydrolyzed product is usually treated with a dilute acid to convert any carboxylate groups to carboxylic acid groups. That is, groups of Formula (VII-B) and/or (VII-C) are usually converted to groups of Formula (VII-A) prior to treatment with the nitrogen-containing compound. That is, the hydrolyzed divinylbenzene/maleic anhydride polymeric material that is reacted with the nitrogen-containing compound has carboxylic acid groups.

The hydrolyzed (e.g., fully hydrolyzed) divinylbenzene/maleic anhydride polymeric material typically has a BET specific surface area equal to at least 50 m<sup>2</sup>/gram or at least 100 m<sup>2</sup>/gram. In some embodiments, the BET specific surface area is at least 150 m<sup>2</sup>/gram, at least 175 m<sup>2</sup>/gram, at least 200 m<sup>2</sup>/gram, at least 225 m<sup>2</sup>/gram, at least 250 m<sup>2</sup>/gram, or at least 300 m<sup>2</sup>/gram. The BET specific surface area can be up to 600 m<sup>2</sup>/gram or higher, up to 500 m<sup>2</sup>/gram, or up to 400 m<sup>2</sup>/gram. In some embodiments, the BET specific surface area is in a range of 50 to 600 m<sup>2</sup>/gram, in a range of 75 to 600 m<sup>2</sup>/gram, in a range of 100 to 600 m<sup>2</sup>/gram, or in a range of 200 to 600 m<sup>2</sup>/gram.

The polymeric sorbent is formed by reacting the hydrolyzed polymeric material having carboxylic acid groups with a nitrogen-containing compound to form an ionic bond. The nitrogen-containing compound, which is usually basic, contains a first primary and/or secondary amino group that reacts with a carboxylic acid group in the hydrolyzed divinylbenzene/maleic anhydride polymeric material. That is, the first amino primary and/or secondary amino group within the nitrogen-containing compound reacts with a carboxylic acid group in the monomeric units of Formula

(VII-A) within the hydrolyzed divinylbenzene/maleic anhydride polymeric material. This reaction results in the formation of an ionic bond linking the nitrogen-containing compound to the polymeric material in the polymeric sorbent. The ionically bonded nitrogen-containing compound has at least one second primary and/or secondary amino group that can react with an aldehyde.

The nitrogen-containing compound has two or more groups of formula  $\text{—NHR}$  where R is hydrogen or alkyl. This compound can have two or more primary amino groups (where R is equal to hydrogen), can have two or more secondary amino groups (where R is equal to an alkyl), or can have at least one primary amino group plus at least one secondary amino group. Suitable alkyl R groups often have 1 to 20 carbon atoms. For example, the alkyl can have at least 1 carbon atom, at least 2 carbon atoms, or at least 4 carbon atoms and can have up to 20 carbon atoms, up to 18 carbon atoms, up to 16 carbon atoms, up to 10 carbon atoms, up to 6 carbon atoms, or up to 4 carbon atoms. In some embodiments, the alkyl has 1 to 10 carbon atoms, 1 to 6 carbon atoms, or 1 to 4 carbon atoms.

Many suitable nitrogen-containing compounds are of Formula (V).



In Formula (V), the group  $\text{R}_1$  is hydrogen or an alkyl. The group  $\text{R}_4$  is a group of formula  $\text{—R}_5\text{—NHR}_6$  or  $\text{—(C=NH)—NH}_2$ . The group  $\text{R}_5$  is an alkylene, (hetero)arylene, (hetero)aralkylene, heteroalkylene having one or more oxy ( $\text{—O—}$ ) groups, or heteroalkylene having one or more  $\text{—NH—}$  groups. (Hetero)arylene and (hetero)aralkylene  $\text{R}_5$  groups can optionally be substituted with a primary amino group and/or a secondary amino group. The group  $\text{R}_6$  is hydrogen, alkyl, or  $\text{—(C=NH)—NH}_2$ .

Suitable alkyl groups for  $\text{R}_1$  in Formula (V) can have at least 1 carbon atom, at least 2 carbon atoms, or at least 4 carbon atoms and can have up to 20 carbon atoms, up to 18 carbon atoms, up to 12 carbon atoms, up to 10 carbon atoms, or up to 6 carbon atoms. In some embodiments, the alkyl has 1 to 10 carbon atoms, 1 to 6 carbon atoms, or 1 to 4 carbon atoms.

In some embodiments,  $\text{R}_4$  in Formula (V) is a group of formula  $\text{—R}_5\text{—NHR}_6$  and the nitrogen-containing compound is of Formula (V-1).

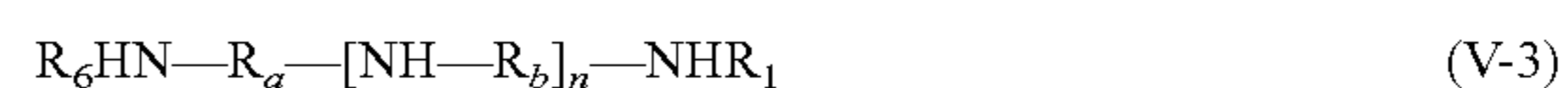


Such compounds have at least two amino groups of formula  $\text{—NHR}$ . Suitable alkyl groups for  $\text{R}_6$  in Formula (V-1) can have at least 1 carbon atom, at least 2 carbon atoms, or at least 4 carbon atoms and can have up to 20 carbon atoms, up to 18 carbon atoms, up to 12 carbon atoms, up to 10 carbon atoms, or up to 6 carbon atoms. In some embodiments, the alkyl has 1 to 10 carbon atoms, 1 to 6 carbon atoms, or 1 to 4 carbon atoms. The group  $\text{R}_5$  can be an alkylene, (hetero)arylene, (hetero)aralkylene, heteroalkylene having one or more oxy ( $\text{—O—}$ ) groups, or heteroalkylene having one or more  $\text{—NH—}$  groups. (Hetero)arylene and (hetero)aralkylene  $\text{R}_5$  groups can optionally be substituted with a primary amino group and/or a secondary amino group.

Suitable alkylene  $\text{R}_5$  groups in Formula (V-1) usually have at least 1 carbon atom, at least 2 carbon atoms, at least 3 carbon atoms, or at least 4 carbon atoms and can have up to 20 carbon atoms, up to 16 carbon atoms, up to 12 carbon atoms, up to 10 carbon atoms, or up to 6 carbon atoms. Some nitrogen-containing compounds are of Formula (V-1) with  $\text{R}_1$  being hydrogen,  $\text{R}_5$  being an alkylene, and  $\text{R}_6$  being

hydrogen. Examples of such nitrogen-containing compounds are alkylene diamines such as, for example, methylene diamine, ethylene diamine, propylene diamine, and butylene diamine. Nitrogen-containing compounds of Formula (V-1) having both  $\text{R}_1$  and  $\text{R}_6$  equal to alkyl include N,N'-dimethylethylene diamine.

In other embodiments of the compounds of Formula (V-1), the group  $\text{R}_5$  is a heteroalkylene (i.e., a heteroalkylene is a divalent radical of a heteroalkane, which is an alkane having catenary heteroatoms) having at least one catenary  $\text{—O—}$  or  $\text{—NH—}$  group. Stated differently, heteroalkylene  $\text{R}_5$  groups have one or more groups of formula  $\text{—R}_a\text{—[O—R}_b\text{]}_n\text{—}$  or  $\text{—R}_a\text{—[NH—R}_b\text{]}_n\text{—}$  where each  $\text{R}_a$  and each  $\text{R}_b$  are independently an alkylene and n is an integer in a range 1 to 50, 1 to 40, 1 to 30, 1 to 20, 1 to 10, 1 to 6, or 1 to 4. Suitable  $\text{R}_a$  and  $\text{R}_b$  alkylene groups often have 1 to 10 carbon atoms, 1 to 6 carbon atoms, 1 to 4 carbon atoms, or 1 to 3 carbon atoms. The heteroalkylene often has up to 30 carbon atoms and up to 16 heteroatoms, up to 20 carbon atoms and up to 11 heteroatoms, or up to 10 carbon atoms and up to 6 heteroatoms. Such nitrogen-containing compounds can be represented by Formulas (V-2) and (V-3).



Some nitrogen-containing compounds are of Formula (V-2) with  $\text{R}_1$  being hydrogen,  $\text{R}_5$  being a heteroalkylene with  $\text{—O—}$  groups, and  $\text{R}_6$  being hydrogen. Examples of such nitrogen-containing compounds are poly(alkylene oxide) diamines such as polyethylene glycol diamine and polypropylene glycol diamine. Further nitrogen-containing compounds are of Formula (V-3) with  $\text{R}_1$  being hydrogen,  $\text{R}_5$  being a heteroalkylene with  $\text{—NH—}$  groups, and  $\text{R}_6$  being hydrogen. Such nitrogen-containing compounds can be, for example, compounds of formula  $\text{H}_2\text{N—[(CH}_2\text{)}_x\text{NH]}_y\text{—(CH}_2\text{)}_x\text{NH}_2$  where x is an integer in a range of 1 to 4 and y is in a range of 1 to 10. Examples include diethylene triamine, triethylene tetramine, and tetraethylene pentamine.

The  $\text{R}_5$  group in Formula (V-1) can also be a (hetero)arylene or (hetero)aralkylene group. The (hetero)arylene or (hetero)aralkylene can optionally be substituted with a primary amino group and/or a secondary amino group. Suitable arylene  $\text{R}_5$  groups often have 6 to 12 carbon atoms and are often phenylene or diphenylene. Suitable heteroarylene  $\text{R}_5$  groups often have 2 to 10 carbon atoms and 1 to 5 heteroatoms selected from nitrogen, oxygen and sulfur. Suitable (hetero)aralkylene  $\text{R}_5$  groups often have an alkylene or alkyl portion having 1 to 10 carbon atoms, 1 to 6 carbon atoms, or 1 to 4 carbon atoms. The aryl or arylene portion of the aralkylene often has 6 to 12 carbon atoms and is often either phenyl or phenylene. The heteroaryl or heteroarylene portion of the heteroaralkylene often has 2 to 10 carbon atoms and 1 to 5 heteroatoms selected from nitrogen, oxygen, and sulfur. In many embodiments, the heteroatoms are nitrogen.

Example nitrogen-containing compounds of Formula (V-1) with both  $\text{R}_1$  and  $\text{R}_6$  being hydrogen and  $\text{R}_5$  being arylene include, but are not limited to, phenylene diamine. An example nitrogen-containing compound of Formula (V-1) with both  $\text{R}_1$  and  $\text{R}_6$  being hydrogen and  $\text{R}_5$  being a heteroarylene is melamine (i.e., melamine is a heteroarylene with three nitrogen heteroatoms, wherein the heteroarylene is substituted with a primary amino group).

Yet other nitrogen-containing compounds are of Formula (V-1) with  $\text{R}_6$  being  $\text{—(C=NH)—NH}_2$  as shown in Formula (V-4).



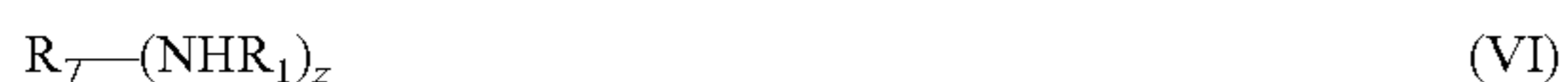
Such compounds have at least two amino groups of formula  $\text{—NHR}$ . In some compounds of Formula (V-4),  $R_1$  is hydrogen and  $R_5$  is alkylene. One such compound is agmatine. Agmatine can be represented by other resonance structures as well but is considered to be within the scope of both Formula (V-1) and (V-4).

In other embodiments of Formula (V),  $R_4$  is a group  $\text{—(C=NH)—NH}_2$ . The resulting compounds are of Formula (V-5).



Such compounds have at least two amino groups of formula  $\text{—NHR}$ . The compound of Formula (V-5) is guanidine when  $R_1$  is hydrogen.

Other suitable nitrogen-containing compounds are polyamines having at least three groups of formula  $\text{—NHR}_1$  where  $R_1$  is hydrogen or alkyl. Such compounds can be of Formula (VI).



In Formula (VI),  $R_1$  is defined as above and the variable  $z$  is equal to at least 3 and can be up to 10, up to 8, up to 6, or up to 4. The  $R_7$  group is often a  $z$ -valent radical of an alkane or a  $z$ -valent radical of a heteroalkane. Suitable  $z$ -valent radicals of alkanes often have a branching carbon atom with at least three of the four adjacent groups being  $\text{—CH}_2\text{—}$ . Suitable  $z$ -valent radicals of heteroalkanes often have a branching nitrogen atom with three adjacent carbon atoms (e.g., three adjacent groups that are alkylene or alkyl groups) or a branching carbon atom with at least three of the four adjacent atoms being carbon (e.g., three adjacent groups that are alkylene or alkyl groups). These  $z$ -valent radicals of heteroalkanes often include one or more groups of formula  $\text{—R}_c\text{—[NH—R}_d\text{]}_p\text{—}$  where each  $R_c$  and each  $R_d$  are independently an alkylene and  $p$  is an integer in a range 1 to 50, 1 to 40, 1 to 30, 1 to 20, 1 to 10, 1 to 6, or 1 to 4. Suitable  $R_c$  and  $R_d$  alkylene groups often have 1 to 10 carbon atoms, 1 to 6 carbon atoms, 1 to 4 carbon atoms, or 1 to 3 carbon atoms. The  $z$ -valent radicals of alkanes often have at least 2 carbon atoms, at least 3 carbon atoms, at least 4 carbon atoms, or at least 5 carbon atoms and up to 20 carbon atoms, up to 16 carbon atoms, up to 12 carbon atoms, or up to 8 carbon atoms. The  $z$ -valent radicals of heteroalkanes often have up to 30 carbon atoms and up to 16 heteroatoms, up to 20 carbon atoms and up to 11 heteroatoms, or up to 10 carbon atoms and up to 6 heteroatoms.

Specific polyamines of formula  $\text{R}_7\text{—(NHR}_1\text{)}_z$  include various polyimines. Some polyimines include one or more branching nitrogen atoms with each nitrogen-branching atom connected to three groups of formula  $\text{—R}_c\text{—[NH—R}_d\text{]}_p\text{—}$ . The end group of each branched segment is often a group of formula  $\text{—NHR}_1$  such as  $\text{—NH}_2$ . Examples include various branched polyethyleneimines. Another specific polyamine is 2-(aminomethyl)-2-methyl-1,3-propanediamine where  $R_7$  is a trivalent radical of an alkane (i.e., the carbon branching atom is connected to four carbon atoms with three adjacent alkylene groups and one adjacent methyl group), each  $R_1$  is hydrogen, and  $z$  is equal to 3.

In many embodiments, the nitrogen-containing compounds such as those of Formula (V) (including Formula V-1 to V-5) and Formula (VI) have a molecular weight (or weight average molecular weight) that is no greater than 2000 Daltons (Da). For example, the molecular weight (or weight average molecular weight) is no greater than 1500 Da, no greater than 1000 Da, no greater than 750 Da, no greater than 500 Da, or no greater than 250 Da.

Up to one mole of the nitrogen-containing compound can be added per mole of carboxylic acid present in the hydrolyzed divinylbenzene/maleic anhydride polymeric material. That is, up to 100 mole percent nitrogen-containing compound can react with the hydrolyzed polymeric material based on the total moles of carboxylic acid. In some embodiments, the amount of nitrogen-containing compound added is up to 95 mole percent or higher, up to 90 mole percent, up to 85 mole percent, up to 80 mole percent, up to 70 mole percent, up to 60 mole percent, or up to 50 mole percent based on the total moles of carboxylic acid. The amount of the nitrogen-containing compound can be at least 1 mole percent, at least 2 mole percent, at least 5 mole percent, at least 10 mole percent, at least 20 mole percent, at least 30 mole percent, at least 40 mole percent, at least 50 mole percent, at least 60 mole percent, or at least 80 mole percent based on the total moles of monomeric units of Formula (II) in the precursor polymeric material. In some embodiments, the amount of nitrogen-containing compound is in a range of 1 to 100 mole percent, in a range of 10 to 100 mole percent, in a range of 20 to 100 mole percent, in a range of 30 to 100 mole percent, a range of 40 to 100 mole percent, in a range of 50 to 100 mole percent, in a range of 60 to 100 mole percent, or in a range of 80 to 100 mole percent based on the total moles of carboxylic acid.

To react the nitrogen-containing compound with the hydrolyzed polymeric material resulting in the formation of an ionic bond, the nitrogen-containing compound is often dissolved in water and/or a suitable organic solvent. Suitable organic solvents are those that dissolve but do not react with the nitrogen-containing compound. Exemplary organic solvents include, but are not limited to, alcohols, ethers such as tetrahydrofuran and diethyl ether, and various chlorinated solvents such as methylene chloride and chloroform. The concentration of the nitrogen-containing compound in water and/or organic solvent can be any suitable amount depending on the solubility of the nitrogen-containing compound. In some embodiments, the concentration of the nitrogen-containing compound in water and/or organic solvent is in a range of 1 to 40 weight percent, in a range of 1 to 30 weight percent, in a range of 1 to 20 weight percent, or in a range of 1 to 10 weight percent.

The solution of the nitrogen-containing compound is mixed with the hydrolyzed polymeric material. The reaction can occur at room temperature or can occur by heating the mixture to a temperature above room temperature. For example, the mixture can be heated at temperatures in a range of 30° C. to 120° C. for several hours to several days. In some embodiments, the suspension is heated at 30° C. to 100° C., 40° C. to 90° C., 50° C. to 90° C., or 60° C. to 80° C. for 12 to 24 hours.

The polymeric sorbent typically has a BET specific surface area that is less than that of the precursor polymeric material. The opening of the anhydride group to form the hydrolyzed polymeric material may sufficiently increase the conformational freedom in the backbone resulting in decreased porosity. In addition, hydrogen bonding between the nitrogen-containing groups in the polymeric sorbent could possibly restrict or block access to pores. Because of this decrease, it is often desirable to prepare a precursor polymeric material having the highest possible BET specific surface area, yet having sufficient anhydride groups to react with the nitrogen-containing compound. The BET specific surface area of the polymeric sorbent is typically at least 25 m<sup>2</sup>/gram.

In some embodiments, the polymeric sorbent further includes an acid-base indicator. The acid-base colorimetric

indicator (i.e., a dye (typically an organic dye) that changes color when it undergoes a transition from being in an acidic form to being in a basic form) can be added at the same time as the nitrogen-containing compound or can be added after addition of the nitrogen-containing compound. The acid-base colorimetric indicator is typically selected to have a  $pK_b$  that is less than a  $pK_b$  of the nitrogen-containing compound. That is, the acid-base colorimetric indicator is selected to change from a first color to a second color when all or a significant portion of the available nitrogen-containing groups on the polymeric sorbent have reacted with an aldehyde. The change in color signals that the capacity of the polymeric sorbent for sorption of an aldehyde has been reached or is close to being reached. As used herein, the term “close to being reached” means that at least 60 percent or more of the capacity has been reached (i.e., a least 60 percent or more of the available sorption sites have been used for sorption of an aldehyde). For example, at least 70 percent, at least 80 percent, at least 90 percent, or at least 95 percent of the sorption sites have been used for sorption of an aldehyde.

Knowing the  $pK_b$  of the nitrogen-containing compound, one of skill in the art can readily select an acid-base colorimetric indicator that has a lower  $pK_b$  value. In some applications, the difference between the  $pK_b$  value of the nitrogen-containing compound and the  $pK_b$  of the acid-base colorimetric indicator is at least 1, at least 2, at least 3, or at least 4. The  $pK_b$  of the acid-base colorimetric indicator is often in a range of 3 to 10.

Example acid-base colorimetric indicators include, but are not limited to, methyl red, bromoxylenol blue, pararosanilin, chrysoidine, thymol blue, methyl yellow, bromophenyl blue, Congo red, methyl orange, bromocresol green, azolitmin, bromocresol purple, bromothymol blue, phenol red, neutral red, naphtholphthalein, cresol red, phenolphthalein, and thymolphthalein.

The acid-base colorimetric indicators can be added to the polymeric sorbent using any suitable method. In some embodiments, the polymeric sorbent is soaked in a solution of the acid-base colorimetric indicator for at least 10 minutes, at least 20 minutes, at least 30 minutes, at least 1 hour, at least 2 hours, at least 4 hours, or at least 8 hours. The solution of the acid-base colorimetric indicator is often in a concentration range of 5 to 10 milligrams per milliliter. Often, about 0.5 grams of the polymeric sorbent is soaked in about 10 milliliters of the solution.

In some embodiments in which an acid-base indicator is present, the role of polymeric sorbent particles **100** may be at least partly, or primarily, to provide a visual indication that a gaseous aldehyde (e.g. formaldehyde) is present in the air to which the polymeric sorbent particles are exposed. That is, a collection of such polymeric sorbent particles **100**, presented on a suitable filter support **10**, might provide a similar function as, for example, the well-known gas detection devices of the type exemplified by Dräger tubes.

In some embodiments, the polymeric sorbent is provided on filter support **100** as a composite, e.g. in the form of granules, that contains a binder along with the polymeric sorbent material for capturing aldehydes such as formaldehyde. The polymeric sorbent material is the same as described above. Such a polymeric sorbent and/or the precursor of the polymeric sorbent included in the composite granules is often prepared in a pressurized reactor as a single block of polymeric material. This block of polymeric material is then broken up and crushed into fine particles using a rotary hammer mill. Typical mills include a screen to help control the particle size by keeping all crushed particles

smaller than the size of the holes in the screen. During the crushing and milling of the polymeric material, a significant amount of fine particles are produced that can be too small for use in some applications such as filtration applications. For example, as much as one third of the polymeric material that is crushed and milled can be too small for use in certain filtration applications. What is considered to be too small can vary depending on the particular application and on the allowable pressure drop.

The fine particles of the polymeric material can be formed into larger particles (i.e., composite granules) by combination with a binder. The composite granules typically have a size that is suitable for use in filtration applications. Thus, formation of the composite granules allows full use of all of the polymeric material formed within the reactor and thereby reduces the overall production costs of the polymeric sorbent.

Furthermore, some processes for making articles (e.g., filtration articles) containing the polymeric sorbents can result in the formation of additional fine particles. For example, making polymeric sorbent loaded webs, loading respirator cartridges, and ultrasonic welding of respirators and respirator cartridges can lead to pulverization of the polymeric sorbent materials resulting in the formation of fine particles. Providing polymeric sorbents in a form that reduces pulverization can be beneficial from a processing perspective. It has been found that combining the polymeric sorbent with a binder can result in the formation of composite granules with improved toughness (e.g., less likely to crumble apart) compared to polymeric sorbent in the absence of a binder. In addition, the composite granules of the present disclosure can be produced without negatively impacting the ability of the polymeric sorbent to sorb aldehyde compounds to such an extent that the composite granules are not useful as sorbents.

The binder included in the composite granules can be an organic material (such as a polymeric material), an inorganic material (such as, for example, a metal silicate salt), or a combination thereof (a compound having an inorganic portion and an organic portion such as, for example, a metal carboxylate salt). In many embodiments, the binder is a salt or a polymeric material such as, for example, a cellulose resin.

In certain embodiments, the binder includes a polyelectrolyte material. Any suitable polyelectrolyte material can be used including those with organic or inorganic counterions. Some suitable polyelectrolyte material is derived from natural polymers or modified natural polymers. Example polyelectrolyte include, but are not limited to, polyamines, polyamides, polyalcohols, polysaccharides, polyacrylamides, polyacrylates, humic acids, proteins, polydiallyldimethylammonium salts such as polydiallyldimethylammonium chloride, polyamine-polydiallyldimethylammonium chloride blends, polyquaternary amines, inorganic-polyamine blends, inorganic-polydiallyldimethylammonium chloride blends, cationic starches, cationic polymethylmethacrylates, copolymers of vinylimidazolium methochloride and vinylpyrrolidone, quarternized vinylpyrrolidone/dimethylaminoethyl methacrylate copolymers, polyethyleneimines, and mixtures thereof. In certain embodiments, the polyelectrolyte material includes cationic starches.

In certain embodiments, the binder includes metal hydroxides, metal oxides, metal salts, organometallic compounds, or combinations thereof. Some suitable metal oxide, metal hydroxide, and metal salt binders are derived from aluminum, calcium, magnesium, or iron (including polyalu-

minum sulfates and polyaluminum chlorides). Other example binders are polyorganozirconates, polyorganoaluminates, polysiloxanes, polysilanes, polysilazanes, polycarbosilanes, polyborosilanes, zirconium dimethacrylate, zirconium tetramethacrylate, zirconium 2-ethylhexanoate, aluminum butoxides, aluminum diisopropoxide ethylacetoacetate, tetramethyldisiloxanes, tris(trimethylsilyl)phosphate, tris(trimethylsiloxy)boron, and combinations thereof. Some example metal salts are metal carboxylate salts such as metal carboxylate salts having 10 to 20 carbon atoms (e.g., magnesium stearate). Other example inorganic binders are silicate salts (e.g., metal silicates). Example metal silicates include sodium silicate (e.g., sodium metasilicate), potassium silicate, calcium silicate, magnesium silicate, and combinations thereof. In certain embodiments, the silicate is sodium metasilicate.

Other example binders include a thermoplastic polymer. The thermoplastic polymer can be selected, for example, from polyamides (such as nylons), polyolefins (such as polyethylenes, e.g., LDPE, LLDPE, HDPE, polyethylene copolymers with other polyolefins, and polypropylenes), polyvinylchlorides (both plasticized and unplasticized), fluorocarbon resins (such as polytetrafluoroethylene), polystyrenes, acrylic resins (such as polyacrylates and polymethacrylates), styrene copolymers (such as acrylonitrile-butadiene-styrenes and acrylonitrile-styrenes), polycarbonates, polyvinylacetates, ethylene-vinyl acetate copolymers, polyvinyl alcohols, polyoxymethylene, polyformaldehyde, polyacetals, polyesters (such as polyethylene terephthalate), polyether ether ketones, and phenol-formaldehyde resins (such as resols and novolacs), and combinations thereof.

Yet other example binders include a thermoset polymer. For example, the thermoset polymer is selected from polyurethanes, silicones, fluorosilicones, phenolic resins, melamine resins, melamine formaldehyde resins, and urea formaldehyde resins.

Still other example binders include an elastomer. In certain embodiments, the elastomer is selected from natural rubbers, synthetic rubbers (such as styrene-butadiene rubber, polychloroprene (neoprene), nitrile rubber, and butyl rubber), silicones, polyurethanes, alkylated chlorosulfonated polyethylenes, polyolefins, chlorosulfonated polyethylenes, perfluoroelastomers, ethylene-propylene-diene terpolymers, chlorinated polyethylene, fluoroelastomers, and mixtures thereof.

In certain embodiments, the binder includes a naturally occurring polymer. Example naturally occurring polymer can be selected from celluloses, collagens, organic acids, and combinations thereof. For example, the naturally occurring polymer can be a biodegradable polymer. Suitable biodegradable polymers can be selected from polyethyleneglycols, polylactic acids, polyvinylalcohols, cellulosic resins (such as cellulose acetate butyrates, carboxy methyl cellulose, and cellulose ethers such as hydroxypropyl methylcellulose), alginic acid, carrageenans isolated from seaweed, polysaccharides, pectins, xanthans, starches, copolymers of polylactideglycolide, and combinations thereof. In some embodiments, the biodegradable polymer is selected from polyethyleneglycols, polylactic acids, polyvinylalcohols, copolymers of polylactideglycolide, and mixtures thereof.

In certain embodiments, the binder includes an electrically conductive polymer. Example electrically conductive polymers can be selected from doped polyanilines and polythiophenes.

In certain embodiments, the binder includes a gelling material, an absorbent material, or combinations thereof.

Example absorbent binder material can be a superabsorbent material such as polyacrylic acids, polyacrylamides, polyalcohols, polyamines, polyethylene oxides, cellulose such as carboxymethyl cellulose, chitins, gelatins, starches, polyvinyl alcohols, polyacrylic acid, polyacrylonitrile, alginic acid, carrageenans isolated from seaweeds, polysaccharides, pectins, xanthans, polydiallyldimethylammonium chloride, polyvinylpyridine, polyvinylbenzyltrimethylammonium salts, polyvinylacetates, polylactic acids, and combinations thereof.

The composite granules often contain binder in an amount of at least 1 weight percent, at least 2 weight percent, at least 5 weight percent, or at least 10 weight percent based on the total weight of the composite granules. In certain embodiments, the binder is present in the composite granules in an amount of up to 30 weight percent, up to 25 weight percent, or up to 20 weight percent, based on the total weight of the composite granules.

The composite granules often contain polymeric sorbent in an amount of at least 70 weight percent, at least 75 weight percent, or at least 80 weight percent, based on the total weight of the composite granules. In certain embodiments, the polymeric sorbent is present in the composite granules in an amount of up to 90 weight percent, up to 95 weight percent, up to 98 weight percent, or up to 99 weight percent, based on the total weight of the composite granules.

In some embodiments, the composite granules contain 1 to 30 weight percent binder and 70 to 99 weight percent polymeric sorbent based on the total weight of the composite granules. For example, the composite granules can contain 5 to 30 weight percent binder and 70 to 95 weight percent polymeric sorbent, 10 to 30 weight percent binder and 70 to 90 weight percent polymeric sorbent, 1 to 25 weight percent binder and 75 to 99 weight percent polymeric sorbent, 5 to 25 weight percent binder and 75 to 95 weight percent polymeric sorbent, 10 to 25 weight percent binder and 75 to 90 weight percent polymeric sorbent, 1 to 20 weight percent binder and 80 to 99 weight percent polymeric sorbent, 5 to 20 weight percent binder and 80 to 95 weight percent polymeric sorbent, or 10 to 20 weight percent binder and 80 to 90 weight percent polymeric sorbent.

The polymeric sorbent and the binder are often blended together without the use of any liquid such as water or an organic solvent. The blended material can then be pressed into a pellet or disk that is subsequently ground or milled and then sieved to obtain composite granules of the desired size (e.g., the composite granules of the desired size are retained on the sieve). Any material that goes through the sieve can be collected and recycled by pressing into additional pellets or disks.

Any suitable pressure can be used to form the pellets or disks. The blended material can optionally be heated during the process of forming the pellets or disks. In some embodiments, the blended material can be heated to a temperature near (but often below) the melting point of the binder. The pressure and temperature are selected to provide pellets or disks that do not crumble (or that undergo minimal crumbling) when broken. The pellets or disks can have any suitable size, such as for example, from 0.5 to 3 centimeters, from 1 to 3 centimeters, or from 2 to 3 centimeters.

The pressure selected for forming the pellets or disks is typically in a range of 6,000 pounds per square inch (psi) to 60,000 psi or even higher. For example, the pressure is often at least 6,000 psi, at least 6,400 psi, at least 6,500 psi, at least 10,000 psi, at least 20,000 psi, or at least 25,000 psi and can be up to 60,000 psi, up to 50,000 psi, up to 40,000 psi, or up to 30,000 psi. The dwell time (the time the force is applied)

can vary from a few seconds to several minutes. For example, the dwell time can be in range of 1 seconds to 10 minutes.

Polymeric sorbents as disclosed herein (whether or not a binder is present) offer a distinct advantage over sorbents based on impregnation of a capture agent. The capture agents are typically simply sorbed on the matrix material such as, for example, activated carbon. That is, the capture agents are usually not ionically attached to the matrix material and can migrate. In contrast, the polymeric sorbents described herein have ionically attached nitrogen-containing groups that interact with the aldehyde and that do not migrate.

The particle size of sorbent particles (whether used alone, or as e.g. composite granules that further include a binder) for use with a filter support (of any type) may vary as desired. In various embodiments, the sorbent particles may have a standard U.S. mesh size (grade) of at least about 4 mesh (i.e., particle size nominally less than 4.8 mm), 6 mesh (particle size nominally less than 3.4 mm), 8 mesh (particle size less than about 2.4 mm), 12 mesh (less than 1680 micrometers), at least about 16 mesh (<1190 micrometers), at least about 20 mesh (<840 micrometers), at least about 40 mesh (<425 micrometers), or at least about 60 mesh (<250 micrometers). In further embodiments, the sorbent particles may have a standard U.S. mesh grade of no greater than about 325 mesh, (i.e., particle size nominally greater than 44 micrometers); 230 mesh (>63 micrometers), 140 mesh (>105 micrometers), 100 mesh (>150 micrometers), 80 mesh (>180 micrometers), 60 mesh (>250 micrometers), 50 mesh (>300 micrometers), or 45 mesh (>355 micrometers).

The skilled person will understand that all of these mesh sizes correspond to nominal grades rather than absolute standards; for example, if a material is described as a 12 mesh material, then approximately 95% or more of the particles will pass through a 12-mesh sieve (and will thus be nominally smaller than about 1680 micrometers in size). If a material is described as 12×20 mesh, then 95% or more of the material will pass through a 12-mesh sieve (i.e. particles smaller than about 1680 micrometers will pass through a 12-mesh sieve) and be retained by a 20-mesh sieve (i.e. particles larger than about 841 micrometers will not pass through a 20-mesh sieve). Mixtures (e.g., bimodal mixtures) of sorbent particles having different size ranges may be employed if desired. Sorbent particles **100** may be processed so as to have any desired particle size distribution. Such processing may include e.g. sieving the particles and/or mechanically grinding the particles as desired.

As noted, the porosity of a polymeric sorbent can be characterized from an adsorption isotherm of an inert gas such as nitrogen or argon by the porous material under cryogenic conditions (e.g., liquid nitrogen at 77 K). The adsorption isotherm is typically obtained by measuring adsorption of the inert gas such as argon by the porous polymeric sorbent at multiple relative pressures in a range of about  $10^{-6}$  to about  $0.98+0.01$ . The isotherms are then analyzed using various methods such as the BET (Brunauer-Emmett-Teller) method to calculate specific surface area and such as Density Functional Theory (DFT) to characterize the porosity and the pore size distribution.

The term “surface area” refers to the total area of a surface of a material including the internal surfaces of accessible pores. The surface area is typically calculated from adsorption isotherms obtained by measuring the amount of an inert gas such as nitrogen or argon that adsorbs on the surface of a material under cryogenic conditions (e.g., liquid nitrogen at 77 K) over a range of relative pressures. The term “BET

specific surface area” is the surface area per gram of a material (typically,  $m^2/\text{gram}$ ) that is usually calculated from adsorption isotherm data of the inert gas over a relative pressure range of 0.05 to 0.30 using the BET method.

In another aspect, a method of sorbing an aldehyde by polymeric sorbent particles **100** as supported on filter support **10** of an air filter **1** is provided. The polymeric sorbent is in the form of particles and includes a reaction product of (a) a hydrolyzed divinylbenzene/maleic anhydride polymeric material having carboxylic acid groups and (b) a nitrogen-containing compound having at least two amino groups of formula  $\text{—NHR}$  where R is hydrogen or alkyl. Any of the polymeric sorbents described above can be used. If desired, the polymeric sorbent can be part of a composite granule.

The polymeric sorbent sorbs aldehydes. Suitable aldehydes are of Formula (I)



where  $\text{R}_2$  is hydrogen, alkyl, vinyl, aryl, or aryl substituted with an alkyl. Suitable alkyl groups typically have 1 to 10 carbon atoms, 1 to 6 carbon atoms, 1 to 4 carbon atoms, 1 to 3 carbon atoms, or 1 carbon atom. The aryl group can have up to 12 carbon atoms or up to 6 carbon atoms. The aryl group is often phenyl. The aryl group can be substituted with an alkyl group such as an alkyl group having 1 to 4 carbon atoms or 1 to 3 carbon atoms.

The aldehyde is sorbed by the polymeric sorbent when it is in the form of a vapor. Thus, the molecular weight of the aldehyde is typically no greater than 200 grams/mole, no greater than 150 grams/mole, no greater than 100 grams/mole, no greater than 75 grams/mole, or no greater than 50 grams/mole. Suitable aldehydes include, but are not limited to formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, pentanal (valeraldehyde), isovaleraldehyde, hexanal, benzaldehyde, 2,5-dimethylbenzaldehyde, 2,4-dimethylbenzaldehyde, 2,3-dimethylbenzaldehyde, tolualdehydes (ortho-tolualdehyde, meta-tolualdehyde, para-tolualdehyde, and mixtures thereof), acrolein and crotonaldehyde. The aldehyde can be sorbed at room temperature or at any desired temperature such as in a range of  $-30^\circ\text{C.}$  to  $150^\circ\text{C.}$ ,  $-30^\circ\text{C.}$  to  $100^\circ\text{C.}$ , or in a range of  $-20^\circ\text{C.}$  to  $50^\circ\text{C.}$

In another aspect, a composition is provided that includes the porous polymeric sorbent particles as supported on a filter support, and an aldehyde sorbed on the porous polymeric sorbent. The polymeric sorbent and the aldehyde are the same as described above. The aldehyde can react with any primary amino group or secondary amino group present on the polymeric sorbent. In some embodiments, the polymeric sorbent is formed using a compound of Formula (V) as the nitrogen-containing compound.



The resulting polymeric sorbent has ionic groups of formula  $\text{—COO}^-(\text{NH}_2\text{R}_1\text{R}_4)^+$ . The anion ( $\text{—COO}^-$ ) is from the hydrolyzed divinylbenzene/maleic anhydride polymeric material and the cation ( $(\text{NH}_2\text{R}_1\text{R}_4)^+$ ) is from the nitrogen-containing compound. Groups  $\text{R}_1$  and  $\text{R}_4$  are the same as defined above.

In some embodiments, the polymeric sorbent is formed using a compound of Formula (V-1) as the nitrogen-containing compound.



The resulting polymeric sorbent can have ionic groups of formula  $\text{—COO}^-(\text{NH}_2\text{R}_6\text{—R}_5\text{—NHR}_1)^+$ ,  $\text{—COO}^-(\text{NH}_2\text{R}_1\text{—R}_5\text{—NHR}_6)^+$ , or both. If the terminal  $\text{R}_1$  of the



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group of formula  $-\text{COO}^-(\text{NH}_2\text{R}_6-\text{R}_5-\text{NHR}_1)^+$  is hydrogen, the polymeric sorbent after exposure to the aldehyde  $\text{R}_2-(\text{CO})-\text{H}$  can have groups of formula  $-\text{COO}^-(\text{NH}_2\text{R}_6-\text{R}_5-\text{NH}-\text{CHR}_2-\text{OH})^+$ ,  $-\text{COO}^-(\text{NH}_2\text{R}_6-\text{R}_5-\text{N}(\text{CHR}_2-\text{OH})_2)^+$ ,  $-\text{COO}^-(\text{NH}_2\text{R}_6-\text{R}_5-\text{N}=\text{CR}_2\text{H})^+$ , or a mixture thereof. Likewise, if the terminal  $\text{R}_6$  of the group of formula  $-\text{COO}^-(\text{NH}_2\text{R}_1-\text{R}_5-\text{NHR}_6)^+$  is hydrogen, the polymeric sorbent after exposure to the aldehyde  $\text{R}_2-(\text{CO})-\text{H}$  can have groups of formula  $-\text{COO}^-(\text{NH}_2\text{R}_1-\text{R}_5-\text{NH}-\text{CHR}_2-\text{OH})^+$ ,  $-\text{COO}^-(\text{NH}_2\text{R}_1-\text{R}_5-\text{N}(\text{CHR}_2-\text{OH})_2)^+$ ,  $-\text{COO}^-(\text{NH}_2\text{R}_1-\text{R}_5-\text{N}=\text{CR}_2\text{H})^+$ , or a mixture thereof. If the terminal  $\text{R}_1$  of the group of formula  $-\text{COO}^-(\text{NH}_2\text{R}_6-\text{R}_5-\text{NHR}_1)^+$  is alkyl, the polymeric sorbent after exposure to the aldehyde  $\text{R}_2-(\text{CO})-\text{H}$  can have groups of formula  $-\text{COO}^-(\text{NH}_2\text{R}_6-\text{R}_5-\text{NR}_1-\text{CHR}_2-\text{OH})^+$ . Likewise, if the terminal  $\text{R}_6$  of the group of formula  $-\text{COO}^-(\text{NH}_2\text{R}_1-\text{R}_5-\text{NHR}_6)^+$  is alkyl, the polymeric sorbent after exposure to the aldehyde  $\text{R}_2-(\text{CO})-\text{H}$  can have groups of formula  $-\text{COO}^-(\text{NH}_2\text{R}_1-\text{R}_5-\text{NR}_6-\text{CHR}_2-\text{OH})^+$ . Additional amounts of aldehyde can react with any remaining primary amino group or secondary amino group.

In yet other embodiments, the polymeric sorbent is formed using a compound of Formula (V-4) as the nitrogen-containing compound.



The resulting polymeric sorbent can have nitrogen-containing groups of formula  $-\text{COO}^-(\text{NH}_3-(\text{C}=\text{NH})-\text{NH}-\text{R}_5-\text{NHR}_1)^+$ ,  $-\text{COO}^-(\text{NH}_2\text{R}_1-\text{R}_5-\text{NH}-(\text{C}=\text{NH})-\text{NH}_2)^+$ , or both. If the terminal  $\text{R}_1$  of the group of formula  $-\text{COO}^-(\text{NH}_3-(\text{C}=\text{NH})-\text{NH}-\text{R}_5-\text{NHR}_1)^+$  is hydrogen, the polymeric sorbent after exposure to the aldehyde  $\text{R}_2-(\text{CO})-\text{H}$  can have groups of formula  $-\text{COO}^-(\text{NH}_3-(\text{C}=\text{NH})-\text{NH}-\text{R}_5-\text{NH}-\text{CHR}_2-\text{OH})^+$ ,  $-\text{COO}^-(\text{NH}_3-(\text{C}=\text{NH})-\text{NH}-\text{R}_5-\text{N}(\text{CHR}_2-\text{OH})_2)^+$ ,  $-\text{COO}^-(\text{NH}_3-(\text{C}=\text{NH})-\text{NH}-\text{R}_5-\text{N}=\text{CR}_2\text{H})^+$ , or a mixture thereof. If the terminal  $\text{R}_1$  of the group of formula  $-\text{COO}^-(\text{NH}_3-(\text{C}=\text{NH})-\text{NH}-\text{R}_5-\text{NHR}_1)^+$  is an alkyl, the polymeric sorbent after exposure to the aldehyde  $\text{R}_2-(\text{CO})-\text{H}$  can have groups of formula  $-\text{COO}^-(\text{NH}_3-(\text{C}=\text{NH})-\text{NH}-\text{R}_5-\text{NR}_1-\text{CHR}_2-\text{OH})^+$ . If the polymeric sorbent has groups of formula  $-\text{COO}^-(\text{NH}_2\text{R}_1-\text{R}_5-\text{NH}-(\text{C}=\text{NH})-\text{NH}_2)^+$ , the polymeric sorbent after exposure to the aldehyde  $\text{R}_2-(\text{CO})-\text{H}$  can have groups of formula  $-\text{COO}^-(\text{NH}_2\text{R}_1-\text{R}_5-\text{NH}-(\text{C}=\text{NH})-\text{NH}-\text{CHR}_2-\text{OH})^+$ ,  $-\text{COO}^-(\text{NH}_2\text{R}_1-\text{R}_5-\text{NH}-(\text{C}=\text{NH})-\text{N}(\text{CHR}_2-\text{OH})_2)^+$ ,  $-\text{COO}^-(\text{NH}_2\text{R}_1-\text{R}_5-\text{NH}-(\text{C}=\text{NH})-\text{N}=\text{CR}_2\text{H})^+$ , or a mixture thereof. Additional amounts of aldehyde can react with any remaining primary amino group or secondary amino group.

In yet further embodiments, the polymeric sorbent is formed using a compound of Formula (V-5)



as the nitrogen-containing compound. The resulting polymeric sorbent can have nitrogen-containing groups of formula  $-\text{COO}^-(\text{NH}_3-(\text{C}=\text{NH})-\text{NHR}_1)^+$ ,  $-\text{COO}^-(\text{NH}_2\text{R}_1-(\text{C}=\text{NH})-\text{NH}_2)^+$ , or both. If the terminal  $\text{R}_1$  of the group of formula  $-\text{COO}^-(\text{NH}_3-(\text{C}=\text{NH})-\text{NHR}_1)^+$  is hydrogen, the polymeric sorbent after exposure to the aldehyde  $\text{R}_2-(\text{CO})-\text{H}$  can have groups of formula  $-\text{COO}^-(\text{NH}_3-(\text{C}=\text{NH})-\text{NH}-\text{CHR}_2-\text{OH})^+$ ,  $-\text{COO}^-(\text{NH}_3-(\text{C}=\text{NH})-\text{N}(\text{CHR}_2-\text{OH})_2)^+$ ,  $-\text{COO}^-(\text{NH}_3-(\text{C}=\text{NH})-\text{N}=\text{CR}_2\text{H})^+$ , or a mixture thereof. If the terminal  $\text{R}_1$  of the group of formula  $-\text{COO}^-(\text{NH}_3-(\text{C}=\text{NH})-\text{NHR}_1)^+$  is alkyl, the polymeric sorbent after

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exposure to the aldehyde  $\text{R}_2-(\text{CO})-\text{H}$  can have groups of formula  $-\text{COO}^-(\text{NH}_3-(\text{C}=\text{NH})-\text{NR}_1-\text{CHR}_2-\text{OH})^+$ . If the polymeric sorbent has groups of formula  $-\text{COO}^-(\text{NH}_2\text{R}_1-(\text{C}=\text{NH})-\text{NH}_2)^+$ , the polymeric sorbent after exposure to the aldehyde  $\text{R}_2-(\text{CO})-\text{H}$  can have groups of formula  $-\text{COO}^-(\text{NH}_2\text{R}_1-(\text{C}=\text{NH})-\text{NH}-\text{CHR}_2-\text{OH})^+$ ,  $-\text{COO}^-(\text{NH}_2\text{R}_1-(\text{C}=\text{NH})-\text{N}(\text{CHR}_2-\text{OH})_2)^+$ ,  $-\text{COO}^-(\text{NH}_2\text{R}_1-(\text{C}=\text{NH})-\text{N}=\text{CR}_2\text{H})^+$ , or a mixture thereof. Additional amounts of aldehyde can react with any remaining primary amino group or secondary amino group.

In still further embodiments, the polymeric sorbent is formed using a compound of Formula (VI) as the nitrogen-containing compound.



The resulting polymeric sorbent can have nitrogen-containing groups of formula  $-\text{COO}^-(\text{NH}_2\text{R}_1-\text{R}_7-(\text{NHR}_1)_{z-1})^+$ . If one of the terminal  $\text{R}_1$  of the group of formula  $-\text{COO}^-(\text{NH}_2\text{R}_1-\text{R}_7-(\text{NHR}_1)_{z-1})^+$  is hydrogen, the polymeric sorbent after exposure to the aldehyde  $\text{R}_2-(\text{CO})-\text{H}$  can have groups of formula  $-\text{COO}^-(\text{NH}_2\text{R}_1-\text{R}_7-(\text{NHR}_1)_{z-2}(\text{NH}-\text{CHR}_2\text{OH}))^+$ ,  $-\text{COO}^-(\text{NH}_2\text{R}_1-\text{R}_7-(\text{NHR}_1)_{z-2}(\text{N}(\text{CHR}_2\text{OH})_2))^+$ ,  $-\text{COO}^-(\text{NH}_2\text{R}_1-\text{R}_7-(\text{NHR}_1)_{z-2}(\text{N}=\text{CR}_2\text{H}))^+$ , or a mixture thereof. If one of the terminal  $\text{R}_1$  of the group of formula  $-\text{COO}^-(\text{NH}_2\text{R}_1-\text{R}_7-(\text{NHR}_1)_{z-1})^+$  is alkyl, the polymeric sorbent after exposure to the aldehyde  $\text{R}_2-(\text{CO})-\text{H}$  can have groups of formula  $-\text{COO}^-(\text{NH}_2\text{R}_1-\text{R}_7-(\text{NHR}_1)_{z-2}(\text{NR}_1-\text{CHR}_2\text{OH}))^+$ . In some of these embodiments, more than one terminal  $-\text{NHR}_1$  group can react with the aldehyde. In addition to the terminal groups, the aldehyde can react with any other primary and/or secondary amino group on the polymeric sorbent.

The amount of aldehyde sorbed by the polymeric sorbent at room temperature (e.g., 25° C.) and standard pressure is often at least 0.5 mmoles/gram (i.e., at least 0.5 mmoles of aldehyde per gram of polymeric sorbent). For example, the amount of aldehyde sorbed can be at least 1 mmole/gram, at least 1.5 mmoles/gram, at least 2 mmoles/gram, at least 2.5 mmoles/gram, at least 3 mmoles/gram, at least 3.5 mmoles/gram, at least 4 mmoles/gram, at least 4.5 mmoles/gram, or at least 5 mmoles/gram. The amount sorbed can be up to 15 mmoles/gram, up to 12 mmoles/gram or even higher, up to 10 mmoles/gram, up to 9 mmoles/gram, up to 8 mmoles/gram, or up to 7 mmoles/gram. The amount sorbed is often in a range of 0.5 to 12 mmoles/gram, in a range of 1 to 12 mmoles/gram, in a range of 2 to 12 mmoles/gram, in a range of 1 to 10 mmoles/gram, in a range of 2 to 10 mmoles/gram, in a range of 3 to 12 mmoles/gram, in a range of 3 to 10 mmoles/gram, or in a range of 3 to 8 mmoles/gram.

Further aspects of the composition and properties, and methods of making and using, of polymeric sorbents as disclosed herein, are presented in U.S. Provisional Patent Application No. 62/520,792, entitled Polymeric Sorbents for Aldehydes, filed even date herewith, which is incorporated by reference herein in its entirety.

#### LIST OF EXEMPLARY EMBODIMENTS

Embodiment 1 is an air filter comprising a filter support that supports polymeric sorbent particles, wherein the polymeric sorbent comprises a reaction product of: a) a hydrolyzed divinylbenzene/maleic anhydride polymeric material having carboxylic acid groups; and b) a nitrogen-containing compound having at least two amino groups of formula  $-\text{NHR}$ ; wherein  $\text{R}$  is hydrogen or alkyl and wherein the nitrogen-containing compound is attached to the hydrolyzed

divinylbenzene/maleic anhydride polymeric material with an ionic bond, and wherein the polymeric sorbent is present in the form of porous particles.

Embodiment 2 is the air filter of embodiment 1 wherein the filter support comprises a substrate with at least one major surface with at least some polymeric sorbent particles disposed thereon.

Embodiment 3 is the air filter of embodiment 2 wherein the polymeric sorbent particles are present substantially as a monolayer on the major surface of the substrate.

Embodiment 4 is the air filter of any of embodiments 1-3 wherein the filter support comprises a porous, air-permeable material with polymeric sorbent particles disposed on a major surface thereof and/or with polymeric sorbent particles disposed within the interior of the material at least in a location proximate the major surface of the material. Embodiment 5 is the air filter of embodiment 4 wherein polymeric sorbent particles are disposed throughout the interior of the porous, air-permeable material.

Embodiment 6 is the air filter of any of embodiments 1-5 wherein the air filter consists essentially of the filter support.

Embodiment 7 is the air filter of any of embodiments 1-6 wherein the filter support comprises a sheet-like material that exhibits a major plane and that exhibits a thickness of less than about 3 mm and that is configured to allow airflow through the filter support at least in a direction at least generally perpendicular to the major plane of the sheet-like material. Embodiment 8 is the air filter of any of embodiments 1-4 and 6-7 wherein the filter support comprises a netting with a major surface with at least some polymeric sorbent particles adhesively attached thereto.

Embodiment 9 is the air filter of any of embodiments 1 and 4-7 wherein the filter support comprises a fibrous web that exhibits an interior and wherein the polymeric sorbent particles are disposed within at least portions of the interior of the web. Embodiment 10 is the air filter of embodiment 9 wherein the polymeric sorbent particles are disposed throughout an interior of the fibrous web. Embodiment 11 is the air filter of any of embodiments 9-10 wherein the web is a nonwoven fibrous web. Embodiment 12 is the air filter of embodiment 11 wherein the nonwoven fibrous web is a meltblown web or a spunbonded web. Embodiment 13 is the air filter of any of embodiments 9-12 wherein at least some fibers of the fibrous web are each bonded to at least one polymeric sorbent particle.

Embodiment 14 is the air filter of any of embodiments 1-5 and 7-13 wherein the filter support is one layer of a multilayer, air-permeable assembly. Embodiment 15 is the air filter of embodiment 14 wherein the multilayer air-permeable assembly includes at least one layer that is not the same layer as the filter support and that is a particle-filtration layer exhibiting a Percent Penetration of less than 50.

Embodiment 16 is the air filter of embodiment 15 wherein the particle-filtration layer comprises electret moieties. Embodiment 17 is the air filter of any of embodiments 1-14 wherein the filter support is a filter media that exhibits a Percent Penetration of less than 50. Embodiment 18 is the air filter of any of embodiments 1-17 wherein the filter support is pleated. Embodiment 19 is the air filter of any of embodiments 1-18 wherein the air filter is a framed air filter that is configured to be inserted into an air filter receptacle of an air-handling apparatus chosen from the group consisting of a forced air heating unit, a forced air cooling unit, a forced-air heating/cooling unit, a room air purifier, and a cabin air filtration unit for a motor vehicle. Embodiment 20 is the air filter of any of embodiments 1, 6, and 14-16

wherein the filter support comprises a honeycomb with through-apertures within which sorbent particles are disposed.

Embodiment 21 is the air filter of any of embodiments 1-5 and 7-17 wherein the filter support provides a layer of a filtering face-piece respirator. Embodiment 22 is the air filter of embodiment 21 wherein the filtering face-piece respirator is chosen from the group consisting of flat-fold respirators and molded respirators. Embodiment 23 is the air filter of any of embodiments 1 and 6 wherein the filter support comprises a container with an interior within which polymeric sorbent particles are disposed, and with at least one air inlet and at least one air outlet. Embodiment 24 is the air filter of embodiment 23 wherein the filter support comprises a filter cartridge. Embodiment 25 is the air filter of embodiment 24 wherein the filter cartridge is configured to be used with a personal protection device chosen from the group consisting of half-face negative-pressure respirators, full-face negative-pressure respirators, escape hoods, and powered air-purifying respirators. Embodiment 26 is the air filter of any of embodiments 1-25 wherein the polymeric sorbent particles are present in granules that further comprise at least one binder.

Embodiment 27 is a method of capturing at least some of an aldehyde from air, the method comprising: positioning an air filter comprising a filter support comprising polymeric sorbent particles of any of embodiments 1-26, so that the polymeric sorbent particles are exposed to the air, and, sorbing at least some of the aldehyde that is present in the air, onto the polymeric sorbent particles; wherein the aldehyde is of Formula (I):  $R_2-(CO)-H$  (I); wherein  $R_2$  is hydrogen, alkyl, vinyl, or aryl and wherein the molecular weight of the aldehyde of Formula (I) is no greater than 200 grams/mole.

Embodiment 28 is the method of embodiment 27, wherein the filter support exhibits a major surface and wherein the air is present in the form of an airstream moving in a direction that is at least generally aligned with a plane of the major surface of the filter support.

Embodiment 29 is the method of embodiment 27 wherein the filter support allows airflow there through and wherein the air is present in the form of an airstream that passes through at least a portion the filter support in a direction at least generally perpendicular to a major surface of the filter support.

Embodiment 30 is a method of making an air filter comprising a filter support that comprises polymeric sorbent particles, the method comprising: (a) providing a divinylbenzene/maleic anhydride precursor polymeric material; (b) hydrolyzing the divinylbenzene/maleic anhydride precursor polymeric material to form a hydrolyzed divinylbenzene/maleic anhydride polymeric material having carboxylic acid groups; and c) reacting the hydrolyzed divinylbenzene/maleic anhydride polymeric material with a nitrogen-containing compound having at least two amino groups of formula  $-NHR$  where R is hydrogen or alkyl to form the porous polymeric sorbent particles, wherein the polymeric sorbent has an ionically attached nitrogen-containing group and wherein the polymeric sorbent particles are porous; and, (d) supporting the polymeric sorbent particles on a filter support.

### 39 EXAMPLES

Materials	
Chemical Name	Supplier
DVB (Divinylbenzene (80% tech grade), which contained 80 weight percent DVB and 20 weight percent styrene-type monomers.)	Sigma-Aldrich, Milwaukee, WI
MA (Maleic anhydride)	Alfa Aesar, Ward Hill, MA
VAZO 52 (2,2'-azobis(2,4-dimethylpentanenitrile))	E. I. du Pont de Nemours, Wilmington, DE
BPO (Benzoyl peroxide)	Sigma-Aldrich, Milwaukee, WI
EtOAc (Ethyl acetate)	EMD Millipore Chemicals, Billerica, MA
NaOH (Sodium hydroxide)	EMD Millipore Chemicals, Billerica, MA
HCl (Concentrated hydrochloric acid, 37%)	EMD Millipore Chemicals, Billerica, MA
EtOH (Ethyl alcohol, denatured, anhydrous)	EMD Millipore Chemicals, Billerica, MA
EDA (Ethylenediamine, 99%)	Alfa Aesar, Ward Hill, MA
DETA (Diethylenetriamine, 99%)	Alfa Aesar, Ward Hill, MA

#### Analysis and Characterization Procedures

Porosity and gas sorption experiments were performed in similar manner to the procedures described in U.S. Provisional Patent Application No. 62/520,792, entitled Polymeric Sorbents for Aldehydes and filed even date with the present application, which is incorporated by reference in its entirety herein.

#### Working Examples 1 and 2

##### Preparation of Divinylbenzene/Maleic Anhydride Precursor Polymeric Material

In a 2 L Parr stainless steel pressure vessel, 177.11 grams (1.09 moles) DVB (80 wt. %, tech grade), 240.05 grams (2.45 moles) of MA, and 4.17 grams (16.8 mmol) of VAZO 52 were dissolved in 625.92 grams of EtOAc. The calculation of moles of DVB used to prepare the precursor polymeric material took into account the purity of the material. The polymerizable composition had 40.0 wt. % solids in EtOAc and contained a monomer mixture (34.0 wt. % DVB, 57.5 wt. % MA, and 8.5 wt. % styrene-type monomers) and 1 wt. % VAZO 52 (based on total weight of monomers). The polymerizable composition was bubbled with nitrogen for 15 minutes. The pressure vessel was then sealed and placed in a water bath at 60° C. The polymerizable composition was heated at this elevated temperature for 18 hours. A white precipitate that had formed was isolated by vacuum filtration and washed with EtOAc. The solid was placed in a 4 L Erlenmeyer flask and 2.0 L of EtOAc was added to the flask. The solid was allowed to stand in EtOAc for one hour at room temperature. The solid was again isolated by vacuum filtration and washed with EtOAc. The solid was placed in a 4 L Erlenmeyer flask and 2.0 L of EtOAc was added. The solid was allowed to stand in EtOAc overnight. The solid was again isolated by vacuum filtration and washed with EtOAc. The solid was then dried in a batch oven at 100° C. for 18 hours. This precursor polymeric material had a BET specific surface area ( $S_{A_{BET}}$ ) of 343.3 m<sup>2</sup>/gram and a total pore volume of 0.593 cm<sup>3</sup>/gram (measured at a partial pressure (p/p°) equal to 0.979) as determined by nitrogen adsorption.

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#### Preparation of Hydrolyzed Precursor Polymeric Material

The precursor polymeric material prepared above was hydrolyzed by treatment with a hydrolyzing agent (NaOH). More specifically, 58.8 g (1.47 moles) of NaOH was dissolved in 490 mL of deionized water within a 1 L jar. To this solution was added 50.0 g of the precursor polymeric material which had been ground and sieved to a particle size range of 40×80 mesh. The jar was then capped and placed on a jar roller. This suspension was allowed to roll at room temperature for 18 hours. The solid was isolated by vacuum filtration and washed with deionized water. The solid was returned to the 1 L jar, and to the jar was added 515 mL of 2.1 M aqueous HCl (80 mL of concentrated HCl added to 435 mL of deionized water). The jar was capped and placed back onto a jar roller where it was allowed to roll overnight at room temperature. The solid was again isolated by vacuum filtration and washed with deionized water. The solid was then dried under high vacuum at 95° C. for eight hours.

#### Amine Functionalization

The hydrolyzed precursor polymeric material prepared above was then reacted with an amine compound containing more than one amino group. The identity of the amine, the amount of amine reacted with the hydrolyzed precursor polymeric material, the equivalents of the amine compound per MA reacted with the hydrolyzed precursor polymeric material, and the concentration of the amine/ethanol (EtOH) solution used for the reaction are summarized in Table 1. More specifically, the amine compound (EDA, DETA) was dissolved into enough EtOH to prepare each amine solution with the concentrations listed in Table 1. To each of these solutions was added 3 grams of the hydrolyzed precursor polymeric material (40×80 mesh particle size). The hydrolyzed precursor polymeric material was allowed to soak in each amine solution at room temperature for 18 hours. The solids were each isolated by vacuum filtration and washed with EtOH. Each solid was then put back in an 8 ounce jar containing 200 mL of EtOH. The solids were allowed to soak in the EtOH for 18 hours. The solids were isolated by vacuum filtration, washed with EtOH, and allowed to dry at room temperature to provide the sorbent particles used to prepare filter samples for formaldehyde capture efficiency testing as described below.

TABLE 1

Sorbent	Amine Type	Amine Amount	Amine Equivalents/MA	Concentration of Amine in EtOH (mol/L)
Working Example 1	EDA	2.0 mL	2	1.5
Working Example 2	DETA	3.8 mL	2	1.2

#### Preparation and Testing of Working Examples

A netting was obtained from Delstar Technologies under the trade designation DELNET R0412-10PR; the netting was reported to have a basis weight of 60 g/m<sup>2</sup>. The netting comprised two sets of filaments oriented substantially perpendicular to each other, to form an array of generally rectangular through-apertures (openings) each with an approximate dimension of 1.7 mm×0.7 mm. A pressure-sensitive adhesive precursor (coating solution) was applied to both sides of the netting and the solvent was dried to leave (an acrylic-based) PSA on each side of the netting at a basis weight of approximately 30 g/m<sup>2</sup> on each side. Working Example 1 sorbent particles (EDA functionalized) were manually sprinkled onto both sides of the netting so that sorbent particles became adhesively attached to the PSA present on the major surfaces of the netting. The sorbent

(including sorbent particles on both sides) was provided at a basis weight of approximately 116 g/m<sup>2</sup>. Similarly, Working Example 2 sorbent particles (DETA functionalized) were manually sprinkled onto both sides of the netting so that sorbent particles became adhesively attached to the PSA present on the major surfaces of the netting. The sorbent (including sorbent particles on both sides) was provided at a basis weight of approximately 138 g/m<sup>2</sup>.

A formaldehyde capture efficiency test was performed on each Working Example 1 and Working Example 2 air filter sample against a challenge of 10 parts per million (by volume) formaldehyde at 50% relative humidity and a 24 LPM air flow (50 ft/min face velocity). Formaldehyde was generated by heating a paraformaldehyde solution in a 50% humid air stream. The formaldehyde concentration was measured using a photoacoustic detector from California Analytical Instruments. A formaldehyde capture efficiency was calculated by % Efficiency = 100 \* (1 - C<sub>downstream</sub> (filter in use) / C<sub>downstream</sub> (filter not in use)) where C is the concentration of formaldehyde in the flowing airstream. FIG. 9 presents (for each air filter/sorbent sample) a plot of formaldehyde capture efficiency as a function of time.

From the formaldehyde capture efficiency plots, a total formaldehyde loading capacity at 95% formaldehyde breakthrough was obtained. This was performed by fitting a line to the plot using standard fitting methods, and extrapolating the line to the x-axis point when the formaldehyde capture efficiency had dropped to 5%. The area under the line was then calculated and was multiplied by the mass flow rate of the formaldehyde and divided by the filter area, to obtain the Formaldehyde Capacity (reported in grams of formaldehyde sorbed per square meter of filter area). The data is summarized in Table 2.

In Table 2, the Test Area is the two-dimensional cross sectional area of circular shaped filter samples (1.75 in (0.0445 m) diameter). The Formaldehyde Efficiency is the efficiency of the sorbent in capturing formaldehyde after 5 minutes of exposure of the sorbent to formaldehyde. Formaldehyde Capacity is the formaldehyde loading capacity at 95% formaldehyde breakthrough, obtained from the above-described procedure. The Sorbent Weight is the loading of sorbent per unit area of the filter sample. The Sorbent Capacity is the Formaldehyde Capacity divided by the Sorbent Weight, so that the Sorbent Capacity is reported (in percent) as mass formaldehyde captured per mass of sorbent used.

TABLE 2

Item	Units	Example 1	Example 2
Test Area	m <sup>2</sup>	0.00156	0.00156
Initial Formaldehyde Efficiency	%	70%	75%
Formaldehyde Capacity	g/m <sup>2</sup>	6.54	10.34
Sorbent Weight	g/m <sup>2</sup>	116	138
Sorbent Capacity	Mass %	5.6%	7.5%

This application incorporates by reference U.S. Provisional Patent Application No. 62/520,792, entitled Polymeric Sorbents for Aldehydes. That application contains numerous Working Examples in which a variety of polymeric sorbents were made and tested in comparison to various Comparative Examples (including activated carbon). Although those Working Examples are not reproduced in this document for reasons of brevity, the characterizations of those Working Example polymeric sorbents in the 79540US002 application would lead the skilled person to

expect that the properties (in particular the enhanced ability to sorb formaldehyde) displayed by those Working Example sorbents would be similarly exhibited were these materials to be disposed on any suitable filter support in the manner disclosed herein.

The foregoing Examples have been provided for clarity of understanding only, and no unnecessary limitations are to be understood therefrom. The tests and test results described in the Examples are intended to be illustrative rather than predictive, and variations in the testing procedure can be expected to yield different results. All quantitative values in the Examples are understood to be approximate in view of the commonly known tolerances involved in the procedures used.

It will be apparent to those skilled in the art that the specific exemplary elements, structures, features, details, configurations, etc., that are disclosed herein can be modified and/or combined in numerous embodiments. All such variations and combinations are contemplated by the inventor as being within the bounds of the conceived invention, not merely those representative designs that were chosen to serve as exemplary illustrations. Thus, the scope of the present invention should not be limited to the specific illustrative structures described herein, but rather extends at least to the structures described by the language of the claims, and the equivalents of those structures. Any of the elements that are positively recited in this specification as alternatives may be explicitly included in the claims or excluded from the claims, in any combination as desired. Any of the elements or combinations of elements that are recited in this specification in open-ended language (e.g., comprise and derivatives thereof), are considered to additionally be recited in closed-ended language (e.g., consist and derivatives thereof) and in partially closed-ended language (e.g., consist essentially, and derivatives thereof). Although various theories and possible mechanisms may have been discussed herein, in no event should such discussions serve to limit the claimable subject matter. To the extent that there is any conflict or discrepancy between this specification as written and the disclosure in any document that is incorporated by reference herein, this specification as written will control.

What is claimed is:

1. An air filter comprising a filter support that supports polymeric sorbent particles, wherein the polymeric sorbent comprises a reaction product of:

- a) a hydrolyzed divinylbenzene/maleic anhydride polymeric material having carboxylic acid groups; and
- b) a nitrogen-containing compound having at least two amino groups of formula —NHR

wherein R is hydrogen or alkyl and wherein the nitrogen-containing compound is attached to the hydrolyzed divinylbenzene/maleic anhydride polymeric material with an ionic bond;

and wherein the polymeric sorbent is present in the form of porous particles.

2. The air filter of claim 1 wherein the filter support comprises a substrate with at least one major surface with at least some polymeric sorbent particles disposed thereon.

3. The air filter of claim 1 wherein the filter support comprises a porous, air-permeable material with polymeric sorbent particles disposed on a major surface thereof and/or with polymeric sorbent particles disposed within the interior of the material at least in a location proximate the major surface of the material.

4. The air filter of claim 1 wherein the filter support comprises a fibrous web that exhibits an interior and wherein

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the polymeric sorbent particles are disposed within at least portions of the interior of the web.

5. The air filter of claim 4 wherein the polymeric sorbent particles are disposed throughout an interior of the fibrous web.

6. The air filter of claim 4 wherein the web is a nonwoven fibrous web.

7. The air filter of claim 4 wherein at least some fibers of the fibrous web are each bonded to at least one polymeric sorbent particle.

8. The air filter of claim 1 wherein the filter support is one layer of a multilayer, air-permeable assembly.

9. The air filter of claim 1 wherein the filter support is pleated.

10. The air filter of claim 1 wherein the air filter is a framed air filter that is configured to be inserted into an air filter receptacle of an air-handling apparatus chosen from the group consisting of a forced air heating unit, a forced air cooling unit, a forced-air heating/cooling unit, a room air purifier, and a cabin air filtration unit for a motor vehicle.

11. The air filter of claim 1 wherein the filter support provides a layer of a filtering face-piece respirator.

12. The air filter of claim 1 wherein the filter support comprises a container with an interior within which polymeric sorbent particles are disposed, and with at least one air inlet and at least one air outlet.

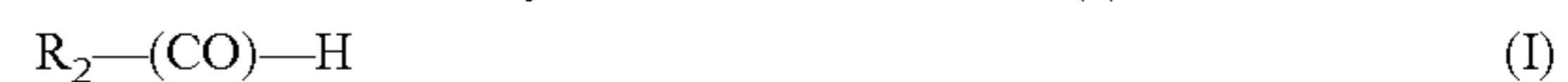
13. The air filter of claim 12 wherein the filter support comprises a filter cartridge.

14. The air filter of claim 1 wherein the polymeric sorbent particles are present in granules that further comprise at least one binder.

15. A method of capturing at least some of an aldehyde from air, the method comprising:  
positioning the air filter of claim 1 so that the polymeric sorbent particles of the air filter are exposed to the air,  
and,

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sorbing at least some of the aldehyde that is present in the air, onto the polymeric sorbent particles  
wherein the aldehyde is of Formula (I)



5 wherein  $R_2$  is hydrogen, alkyl, vinyl, or aryl and wherein the molecular weight of the aldehyde of Formula (I) is no greater than 200 grams/mole.

16. The method of claim 15, wherein the filter support exhibits a major surface and wherein the air is present in the form of an airstream moving in a direction that is at least generally aligned with a plane of the major surface of the filter support.

17. The method of claim 15 wherein the filter support allows airflow therethrough and wherein the air is present in the form of an airstream that passes through at least a portion the filter support in a direction at least generally perpendicular to a major surface of the filter support.

18. A method of making an air filter comprising a filter support that comprises polymeric sorbent particles, the method comprising:

- (a) providing a divinylbenzene/maleic anhydride precursor polymeric material;
  - (b) hydrolyzing the divinylbenzene/maleic anhydride precursor polymeric material to form a hydrolyzed divinylbenzene/maleic anhydride polymeric material having carboxylic acid groups; and
  - (c) reacting the hydrolyzed divinylbenzene/maleic anhydride polymeric material with a nitrogen-containing compound having at least two amino groups of formula  $NHR$  where  $R$  is hydrogen or alkyl to form the porous polymeric sorbent particles, wherein the polymeric sorbent has an ionically attached nitrogen-containing group and wherein the polymeric sorbent particles are porous;
- and,
- (d) supporting the polymeric sorbent particles on the filter support.

\* \* \* \* \*